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Part I
Long Term Leaching Potential Of Oil Contaminated Cuttings in the Arctic Marine Environment

Part II
Oxygen Demand of Oiled Drill Cuttings

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Northern affairs Program

Part I

Long Term Potential for Leaching
of Oil Contaminated Cuttings from
the Use of Oil Based Muds in the
Arctic Marine Environment

Final contractual report by:
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Dobrocky Seatech Ltd.
for
Indian and Northern Affairs Canada
september, 1986

Part II

Oxygen Demand of Oiled Drill Cuttings

Final contractual report by:
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Long Term Potential for Leaching of Oil Contaminated Cuttings from the Use of Oil Based Muds in the Arctic Marine Environment

Final contractual report by
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Dobrocky Seatech Ltd.
for
Indian and Northern Affairs Canada
September, 1986

ABSTRACT

This report describes the experimental investigation of the rates and durations of release of oil and oil fractions from low aromatic mineral oil contaminated drill cuttings discharged to static (under ice) and dynamic (openwater, wave) arctic marine environments. Experimental and analytical protocols are described and results are presented. The rates of hardening and consolidation (cuttings pavement formation) of the cuttings layers under static and dynamic conditions were also investigated. The wave regime was found to be the dominating influence in the experiments conducted; the oil concentrations on the cuttings were significantly affected by the presence of waves.

KEY WORDS

Arctic Marine Environment; Beaufort Sea; Marine Drilling; Marine Pollution; Oil; Oil and Gas Industry; Oil Contaminated Drill Cuttings; Pavement Formation.

RÉSUMÉ

Ce rapport décrit les études expérimentales portant sur les vitesses et les durées de rejet de pétrole et de fractions tirées du pétrole provenant des déblais de forage contaminés par de l'huile minérale à faible teneur en produits aromatiques, déversés en eaux marines statiques (sous la glace) et dynamiques (à la surface en présence de vagues) en milieu arctique. On décrit les protocoles expérimentaux et analytiques et on présente les résultats obtenus. On examine aussi la vitesse de durcissement et de consolidation (formation d'une couche indurée) des couches de déblais en conditions statiques et dynamiques. L'intensité des vagues avait un effet dominant dans les expériences réalisées; les vagues influaient beaucoup sur la concentration de pétrole sur les déblais.

Mots clés

Environnement marin arctique; mer de Beaufort; forage en milieu marin; pollution marine; pétrole; industrie pétrolière et gazière; déblais de forage contaminés par le pétrole; formation d'une couche indurée à partir des déblais de forage.

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SUMMARY

This report includes a detailed review of pertinent literature on the fate and effects of oil-based muds. Environmental observations of oil-based muds discharged to the marine environment are summarized for both North Sea and Canadian Scotian Shelf studies. Existing information (including some very recent North Sea data) on the weathering and biodegradation of oil-based mud cuttings is also reviewed. The effects of marine discharges of oiled mud cuttings on the arctic environment are also hypothesized based on the results of studies conducted to date.

The objectives of this experiment were to perform laboratory studies to determine (a) the approximate rates and durations of release of oil from contaminated oil-based mud drilling cuttings and, (b) the potential formation of a surface crust on an oil contaminated drilling cuttings pile. Experiments were to be conducted in a static environment and in a wave environment typical of Beaufort Sea drilling locations. Oil-based drilling mud cuttings using Vista ODC (formerly Conoco ODC) base oil from the Beaufort Sea Adgo G-24 well site were used for the experiments.

The experimental facility was constructed in an unheated portable trailer on the foreshore of Patricia Bay (near Sidney, B.C.), across the road from the Dobrocky Seatech Ltd. facilities. The two test tanks (static and wave) were cooled by immersing in an ice bath and the experiment was run for 49 days. Samples were collected of the intake water and of the outlet water from each tank. In most cases triplicate samples of the cuttings were collected on each sampling day. A random number generator was used to select locations for sampling in each tank and the area within 5 cm of the walls was avoided to eliminate any influence of the tank walls on the samples. Qualitative sediment penetrometer measurements were also taken in

effort to document changes in the hardness of the cuttings surface. The cuttings in the static tank were undisturbed by any turbulence or wave action and the relatively low water replacement rates (1 L/min or one water change every 10-12 h) ensured that water flow through the static tank was very close to laminar. Size limitations on the height of the tanks and the wave damper provided an upper limit on the wave amplitude. As a result, the reflected wave had approximately one-half the amplitude of the incident wave and this was felt to provide a good model of the situation windward of an artifical island or solid drilling structure. The water depth modeled (23 m) was also typical of the water depths at many of the Beaufort Sea drilling sites.

The oiled cuttings were loose and unconsolidated in both tanks at the beginning of the experiment and were essentially unchanged after 49 days exposure in the static tank. In the wave tank after 49 days the surface cuttings were loose with a "jello-like" consistancy, but in the subsurface layers of the cuttings mass, they were dense and very cohesive. This bottom material was hard and compact and could be described as a "bottom pavement". The sediment penetrometer showed a gradual decrease in cuttings surface resistance in the static tank and a gradual increase in resistance in the wave tank. Since the penetrometer measurements applied only to the surface layers, the formation of a "bottom pavement" in the wave tank was not detected by the penetrometer technique. The two tanks showed essentially the same temperature regime and mean temperature (5 ± 2°C) throughout the experiment.

In the static tank, the cuttings surface oil concentrations showed an initial increase as oil floated to the top of the cuttings pile (the base oil is about 0.23 kg/L less dense than seawater) and then remained relatively constant throughout the experiment. The water samples showed an initial massive release of oil (with an oil in water concentration of 1.5% on Day 0) followed by a relatively steady low part per million oil level.

Since the water samples were collected from the surface runoff from each tank, the amount of oil measured was dominated by the number of surface oil drops that happened to be collected with the sample. The static tank cuttings samples collected on Day 49 showed no significant difference by t-test in the oil content of the surface and subsurface samples.

In the wave tank, the cuttings surface oil concentrations increased to a maximum of about 3.5 times the initial oil concentration at a point about half-way through the experiment and then decreased to a level just above the initial concentration. Throughout most of the experiment, cuttings surface oil concentrations were much greater in the wave tank than in the static tank. Surface water oil concentrations in the wave tank were however in general lower then in the static tank and fell below the limit of detection approximately half-way through the experiment. The large Day 0 difference between the surface oil concentrations measured in the static and wave tanks was attributed to substantial differences in the amount of "free" oil present in each tank at the point when the water was added. The wave tank cuttings samples collected on Day 49 showed a significant difference (t-test) in oil content between the surface and subsurface samples with the surface samples having significantly higher oil concentrations.

Non-parametric two-way analysis of variance testing showed that the cuttings oil concentrations were significantly affected by the presence of waves. However on the average, when both tanks were considered together, the cuttings surface oil concentratons did not change with time during the experiment. It was presumed that the lack of change in the static tank had influenced the results of this test and the hypothesis was retested for the wave tank alone. This time the testing indicated that the cuttings surface oil concentrations did change significantly with time during the experiment in the wave tank.

Other statistical tests showed no correlation between the surface oil concentrations and the wave particle velocities at each sampling position which indicated that the partial (18%) reflection of the generated wave had

no measurable effect on the oil concentrations. It was concluded that any changes in temperature observed during the experiment had a negligible effect when compared to the profound effects of waves relative to a static exposure.

Gas chromatography (GC) analysis was used to study the compositional changes in the base oil during the experiment. All of the GC traces run of static tank cuttings samples showed essentially the same trace as the pre-experiment sample. Similarly all of the wave tank surface cuttings samples except two showed this same GC trace. These two samples and all three of the subsurface cuttings samples collected on Day 49 from the wave tank showed a marked change in the GC trace with hydrocarbons in the range of nonane (n-C9) to undecane (n-C11) being missing from the samples. This loss was attributed to the preferential leaching of a discrete lower boiling fraction of the base oil out of the subsurface layers of the cuttings pile. It was also concluded that this process was accelerated by wave action. In addition, since the subsurface hydrocarbon concentrations were significantly lower than the surface concentrations in the wave tank, it was concluded that this fractionation was accompanied by a general loss of oil from the subsurface cuttings layers.

The changes in the oil composition of the water samples were dominated by droplets of unweathered oil masking other changes. When the oil concentrations were high, then the GC trace was essentially the same as the trace of the base oil. However as the oil concentration dropped and a larger fraction of the oil was dissolved or emulsified in the water, the GC trace showed more "weathering" with a reduction in the resolved fraction and a shift in the mean hydrocarbon size to a higher molecular weight.

In conclusion it can be said that a wave regime was the dominating influence in the experiments conducted. It can be expected that oiled mud cuttings discharged in the shallow arctic during open water will be strongly influenced (leached or weathered) by wave action (and in particular by summer storms). Cuttings discharged through the ice after freeze up and/or into deep water can be expected to show only the low loss

of oil typical of the static regime of this experiment and can be expected to persist for extended periods of time on the sea floor. The inference is that the environmental impact of the discharge of oiled cuttings will be less if the cuttings are discharged into shallow water where they will be influenced by waves and storm events.

The results of this experiment suggest that "bottom pavement" formation is part of the process of the loss of oil from the drilling cuttings, although it may also be linked to compaction of subsurface material by wave action. The presumption could be made that the "bottom pavement" would erode away once all of the oil was gone, but this experiment did not continue long enough to prove this supposition.

RECOMMENDATIONS

Since the wave exposure had a much greater effect on the oiled cuttings than the static exposure, it is felt that there is little to be gained by more static experiments and further work should concentrate on defining the effects of the wave regime. Static exposure experiments can only be expected to model the very deep water or under ice regime and will thus be of limited use for the Beaufort Sea.

It is recommended that more wave experiments be conducted and extended for a longer period of time than the 49 days of this experiment. A few different wave regimes should be used to derive a good predictive model; higher wave energies than were possible in this experiment should be used and at least one "storm" event should be studied. The modifications to a facility like the one used for this experiment would not have to be extensive to carry out these studies. A longer and deeper wave tank would be required and an adjustable wave generator should be used. The use of an external cooling unit would provide better temperature control and allow operation of the experiment in different parts of the year.

A quantitative measurement of oiled cuttings resistance in both the surface and subsurface layers of a cuttings pile may be beyond present technology and hence its inclusion in future experiments is not strongly recommended. In subsequent work, thought should also be given to collecting subsurface water samples by a resin preconcentration method, so that the compositional changes can be studied. In addition, if the outflow oil absorbant from each tank is collected, dried and weighed periodically, then it would be easier to calculate a budget for oil loss.

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1.0 INTRODUCTION

The objectives of this experiment were to perform laboratory studies to determine a) the approximate rates and durations of release of oil from contaminated oil-based mud drilling cuttings and, b) the potential formation of a surface crust on an oil contaminated drilling cuttings pile.

To achieve the experiment objectives, the following tasks were requested:

a) To collect, describe and summarize, in the form of a literature review, all appropriate information on the rates and durations of release of oil, and the fate of oil fractions from contaminated cuttings;

b) To design an experimental protocol to determine the rates and durations of release of oil and oil fractions from the contaminated cuttings, based on the literature review and relevance to the Canadian arctic marine environment;

c) To implement the experiment to allow for the comparison of the rates and durations of release of oil fractions from the contaminated cuttings in a static and typical wave energy environment; and,

d) To conduct a series of measurements on the oil contaminated cuttings in the static and wave environments to estimate the rate of hardening and consolidation. The final experimental design was to be determined in consultation with the Scientitic Authority.

The final experimental design was also to simulate as much as possible (with the resources available) the typical physical and chemical Beaufort Sea conditions such as mixing energy, temperature and salinity, at typical Beaufort Sea drilling locations.

2.0 REVIEW OF PERTINENT LITERATURE ON THE FATE AND EFFECTS OF OIL-BASED MUDS

2.1 GENERAL CONSIDERATIONS

The fate of drilling fluids and cuttings discharged into the marine environment is determined by diverse physical processes e.g. wave climate, currents, dissolution of soluble components), chemical processes (chemical reaction, sorption onto particulates) and biological processes (incorporation into the food web) that all serve to disperse, change or concentrate constituent materials (National Academy of Sciences, 1983). These materials are distributed by the dispersive energy of the ocean at the discharge site which, in turn, is a function of wind, tide and mean currents. Dispersion will vary with site location and water depth because of the factors which influence the turbulence and thus mixing in the water column and in the bottom boundary layer. These factors include:

- wind-driven and tidal currents;
- wave climate;
- ice cover and bottom scouring by ice;
- vertical density stratification (temperature and salinity);
- presence of suspended sediments;
- variable seabed conditions (bioturbation, bed forms, and near-bed transport); and,
- storm events.

In the case of cuttings discharges, the relatively large particles will settle rapidly near the point of discharge. Soluble and particulate fluid additives adhering to the cuttings will, to some extent, be washed off as the larger particles settle. The distance the cuttings travel from the well-site and the settlement time have been found to be primarily a function of current speed and water depth (Ayers et al., 1980).

Once the cuttings have been dispersed by the prevailing currents, the major energy source for their resuspension and dispersion is likely to be wave action. In waters deeper than 20 m and/or in areas that are ice-covered for large portions of the year, the likelihood of cuttings being significantly dispersed by wave action decreases. In the deeper water drilling areas of the high Arctic, for example, the bottom sediments will rarely, if ever, be influenced by wave action.

2.2 ENVIRONMENTAL OBSERVATIONS OF OIL-BASED MUDS DISCHARGED TO THE MARINE ENVIRONMENT

2.2.1 North Sea Studies

The majority of the studies on environmental effects of discharged oil-based cuttings come from the North Sea. There is virtually no comparable information on Arctic areas, although some experimental studies are currently in progress.

The conclusions of a United Kingdom working group on the environmental effects of oil-based mud (OBM) cuttings are pertinent to this discussion (Davies et al., 1984a). They found that despite both differences in inputs from different platforms and the variations in benthic topography at different locations, the benthic chemical and biological effects associated with these discharges could be summarized in terms of four zones of differing impact.

Zone I (Davies et al., 1984a) is typified by an impoverished and highly-modified benthic community (see Table 2.1). Beneath, and in the immediate vicinity of the platform, biological effects are due mainly to physical burial of the natural sediment which can lead to anaerobic conditions. A number of workers have noted that OBM cuttings are cohesive and undergo very little resuspension (Blackman and Law, 1981). In the laboratory, it was found that when diesel-based cuttings had an oil content of greater than 4-5% by weight, even those containing angular sand grains aggregated into large pellets which sank rapidly (100-700 m/hr). The authors concluded that very little absorbed oil was stripped from the solids during settlement but that, after deposition, oil continued to leach slowly to the surrounding water.

Table 2.1 Zones of Impact For The Environmental Effects of Discharge of Oil-Based Mud and Cuttings (Davies et al., 1984a).*

Zone	Maximum Extent Within Range	Biology	Chemistry
I	0 - 500 m (usually <250m)	Impoverished and highly modified benthic community (beneath and very close to the platform the seabed can consist of cuttings with no benthic fauna)	Hydrocarbon (HC) levels high. Sediments largely anaerobic. HC's 1,000 plus x background.
II	200 - 2,000 m	Transition zone in benthic diversity and community structure.	Hydrocarbon levels above background. HC's 10 - 700 x background.
III	800 - 4,000 m	No benthic effects detected.	Hydrocarbon levels return to background. HC's 1 - 10 x background.
IV	> 4,000 m	No benthic effects	No elevation of hydrocarbons.

* This study considered diesel and first generation (i.e., high aromatic) low toxicity base oils only.

The authors reported that oiled cuttings can be compacted to form a bottom pavement and as little as 1 cm of cuttings can have the effect of sealing off the natural sediments. Around the discharge point, the seabed can consist of cuttings with no benthic macrofauna and sediment hydrocarbon concentrations usually exceeding 1,000 times background. In most cases studied, Zone 1 was confined to within 250 m although an outer limit of 500 m was used to include all fields.

In all North Sea fields studied up to the time of the review, the major deleterious biological effects were confined to within the 500 m zone and were associated primarily with (i) burial under the cuttings on the seabed (immediately adjacent, <100 m, to the platform) and (ii) the organic enrichment associated with the spread of oil from the cuttings. Seabed recovery in this first zone is likely to be a long process with layers of compacted cuttings persisting on the seabed for several years in deep water areas.

Surrounding the area of major impact is a transition zone (Zone II) in which subtle biological effects can be detected as community parameters return to normal, generally within 200 to 1,000 m. The benthic community exhibits a classic successional response to point source organic pollution, with a peak of opportunist species occurring in the immediate vicinity of the platform. These species are very important since their abundance and high levels of productivity play an important role in the breakdown of organic pollutants. In this regard, several correlations between chemical and biological parameters (such as sedimentary oil content and species abundance and the diversity/number of individuals) have been reported (Davies et al., 1984a; IOE, 1985a).

The shape and extent of this zone is variable, and is largely determined by the current regime and the scope of the drilling operation. With increasing current velocities and more extensive drilling, this delineation may be extended to 2,000 m in the direction of residual current. From the little information available, the surface sediments studied in this zone appeared to be aerobic and biodegradation of hydrocarbons seemed to be taking place. A more rapid recovery of the transition zone was expected on cessation of drilling.

In Zone III (800-4,000 m) elevated hydrocarbon concentrations attributable to OBM were detected but no biological effects could be found.

Zone IV was the area beyond 4,000 m and no chemical or biological effects could be observed. Generally speaking, background levels were reached within 3,000 m, although this was extended for fields which produced very fine cuttings. In certain areas of the North Sea where offshore production platforms have recently been, or are about to be installed, it is no longer possible to find the "background" levels of sedimentary hydrocarbons that were observed 5-10 years ago. Extensive oil production activity in the East Shetland Basin, for example, appears to be producing elevated levels of sedimentary hydrocarbons to the south of this region.

The spread of cuttings has been found to be greatly influenced by particle size. Cuttings resulting from the use of OBM are generally larger than when using WBM (water-based mud) and tend to fall, as agglomerations, more directly to the seabed. The U.K. Committee also found that the extent of biological effects was greater from OBM cuttings than from WBM cuttings beyond the area of physical smothering (e.g., Zones II and III). These effects of oil-contaminated cuttings may be due to organic enrichment of the sediment and/or toxicity of certain fractions such as aromatic hydrocarbons. It was estimated that sediment oil concentrations of 100 ppm diesel, or 2 ppm naphthalenes, would be expected to restrict many species of benthic organisms (Armstrong et al., 1979).

Davies et al. (1984a) noted that there will be an overlap between the zones in both distance and pollutant levels and that the true picture will be a gradient of change away from the platform. The pattern of cuttings deposition reflects several factors including the prevailing current regime, depth of water, and height of the discharge point above the sea bed. The distances in Table 2.1 represent the maximum extent of the zones visualized at that time (1983), although this is currently under review.

The concept of "zones of effect" proved useful as a basis for summarizing the existing impacts as of 1982-83. With the large number of highly-deviated wells being drilled from one platform in the northern North Sea, and the increasing use of OBM throughout most drilling programs, it may be that the "maximum extent of the highly-modified benthic community" (Davies et al., 1984a) will not be contained within a 500 m zone. Similarly, whether the "benthos returns to normal" for the majority of the North Sea fields within 1,000 m remains to be conclusively proven, and the distance at which no benthic effects or elevation of hydrocarbon levels is reached is still to be firmly established.

Long-term recovery of an area following the cessation of discharge is likely to be affected by a number of factors including (Davies et al., 1984a):

(a) redistribution and spreading of cuttings;
(b) biodegradation or dissolution of the oil on the cuttings;
(c) burial of the cuttings and recolonization of the surface sediment.

2.2.2 Scotian Shelf Field Results

A study funded by ESRF, on the distribution of low toxicity oil-based mud cuttings discharged at two Sable Island, Nova Scotia, wellsites supported the general conclusions of the United Kingdom studies (Davies et al., 1984a) for a deep water (70 m) site, but found that the U.K. experience would have overestimated the impact for a shallow water site (Yunker and Drinnan, 1986).

The two well sites studied were substantially different. One was located in about 16 m of water along the south side of the eastern bar of Sable Island, an area where bottom sediments were well-mixed by wave action. The other site was located about 19 km north of the middle of Sable Island, in about 70 m of water. At this site, the bottom sediments were influenced primarily by tidal currents during the study period.

At the shallow water site, hydrocarbon concentrations were observed to drop off to a level 10 times above background at approximately 200 m from the wellsite. In comparison with the U.K. summary (Table 2.1), this would mean that Zone II (the transition zone) and Zone I (the impoverished zone) extended less than 200 m from the wellhead. By extrapolation, the region of severe benthic biological impact would be within the 200 metre contour, although no grab samples were taken in that region. At this well, however, divers noted that the cuttings mound was only 20-25 m across. By inference, it is expected that the impacts will be much less than those predicted by the U.K. summary. The reasons for this are due to the active sediment movement and redistribution, similar to that expected in the shallow southern Beaufort Sea during the summer. Note, however, that the well was a single, exploratory well while the U.K. results are based on multi-well discharges.

At the deep water site, however, the study results were much closer to those predicted by the U.K. summary. At this well, the hydrocarbon levels dropped to 10 times above background (the beginning of Zone III, no benthic effects, see Table 2.1) at distances ranging from 200 to 1500+ m from the wellhead. Hydrocarbon concentrations fell to two orders of magnitude above background (approximately Zone II, the transition zone) at distances ranging from about 150 to 650 m from the wellsite. Concentrations three orders of magnitude above background (Zone I, the impoverished zone) were present (depending on direction) at distances closer than about 100 to 400 m from the well.

Samples collected at the wellhead at both sites, had aliphatic hydrocarbon concentrations that were five orders of magnitude above background. However, at the shallow site, the cuttings mound, which orginally was deposited in a compact pile (24 m x 20 m, 30 cm deep) under the drilling rig, was completely dispersed within a few months (diver observations). At the deeper wellsite, substantial amounts of oiled cuttings were found in the region of the wellhead during post-drilling sampling even though the discharge of cuttings had stopped nearly a month earlier.

2.3 WEATHERING AND BIODEGRADATION OF OBM

Visual and laboratory observations (Blackman and Law, 1981) indicate that most diesel oil-based cuttings are very cohesive and this aggregation of particles can be expected to require high water velocities for suspension. However, there is some evidence of a hydrocarbon weathering gradient away from a platform. Saltzmann (1982) found a change in the ratio of the parent compound and substituted naphthalenes with increasing distance from the Beryl A platform in the North Sea, and increasing weathering of aliphatic hydrocarbons with distance from the platform was demonstrated along the northwest transect from the Thistle platform in 1982, both of which suggest a gradual movement of the cuttings away from the platform (Davies et al., 1984a). The drill cuttings study on the Scotian Shelf (see previous section), has also indicated that weathering of the hydrocarbons in sediments (up to n-C12) occurred, particularly in areas of considerable sediment mixing.

There are relatively few quantitative field studies of biodegradation of hydrocarbons in sublittoral sediments. From the evidence available (Saltzmann, 1982; Jones et al., 1983) it would appear that in the water column and in the surface sediments of the aerobic Zones II and III, the small aliphatic and aromatic (naphthalenes) molecules will be biodegraded quite quickly but that the large 3, 4 and 5 ring aromatics may be biodegraded two or three orders of magnitude more slowly (Massie et al., 1985).

Details of a laboratory study of the oxygen demand of oiled drill cuttings layered over natural marine sediments have been reported by Hutcheson et al. (1985). The total sedimentary oxygen demands (over a 30-day period) of low toxicity oil-based drill cuttings (Conoco ODC) layered over both fine and coarse marine sediments in 1, 2.5, 5 and 15 mm layers were measured in conjunction with redox potential (Eh) profiles and levels of selected trace metals in both pore waters and sediments. Based on a series of measurements of oxygen demand over the 30-day study period Hutcheson and co-workers were able to derive multiple regression equations to predict the

oxygen demands of cuttings on both coarse and fine sediments, with time (days) and cuttings thickness (mm) as independent variables.

Redox potentials ranged from 310-601 mV. No negative potentials were recorded and no vertical Eh gradients were observed through cuttings into coarser sediments. The study also indicated that mobilization of Hg, Pb, Cd and Zn should not occur under conditions similar to those in the experimental program. Mobilization of Cu, however, did appear to occur. With larger decreases in Eh it was noted that other changes in pore water chemistry could have occurred.

In Zone I (in areas of low wave action) anaerobic conditions will prevail just below the surface of the cuttings pile and little or no biodegradation is likely below the surface bacterial layer. Under these circumstances capping of the cuttings by local sediment resuspension and deposition, and subsequent recolonization of the area in the aerobic deposit, seems the most likely mechanism of recovery (Davies et al., 1984a).

It has been observed that direct leaching of oil from cuttings into sea water appears to be very slow (Engelhardt et al., 1983) with initial rates of 0.1% of total oil per day and total losses in the order of 1-4% of total oil over a "substantial period of time" being quoted. Poley and Wilkinson (1983) have suggested that, from laboratory studies, leaching rates of "oil from cuttings" (neither described) would be approximately 2 g/m^3/day. In preliminary experiments, Doe (1984) conducted static exposures of oiled cuttings from a Canadian East Coast well to seawater. No significant release of oil from the cuttings was demonstrated at 4°C over the 31 day period of the experiment; increasing the cuttings surface area by over an order of magnitude did not affect this result. Note that in the latter experiment, no attempt was made to measure seawater oil concentrations and the changes in cuttings oil concentrations were likely too small to measure. These experiments indicate that very little change in oil concentration is to be expected in the experiments carried out in this study.

Further laboratory experiments by Shell UK Exploration and Production (DeJong, 1983) have shown relatively high rates of oil release from

"unwashed cuttings" (not described) followed by a slow, steady release of oil, but with a subsequently similar release rate of approximately 1 $g/m^3/day$. In spite of this apparent lack of availability, accumulation of non-polar hydrocarbons from low toxicity oiled cuttings has been observed to occur in parallel with lethal response in a few marine invertebrates tested (Hutcheson et al., 1984). The possible implications of this uptake on potential fish tainting have not been fully investigated, although recent reports from the Danish sector of the North Sea give some indications of petroleum tainting of flatfish caught in the regions adjacent to oil production areas (Robson, 1986, pers. comm.).

Complete burial of the benthic fauna beneath and immediately adjacent to the drilling platform will occur as a result of the discharge of both diesel and low toxicity oil-based mud cuttings and there is little evidence that the low toxicity oil-based mud cuttings will have less overall impact on the seabed. The hydrocarbon load of low toxicity oil-based mud cuttings results in significant organic enrichment of the seabed (Addy et al., 1983). Within the organically-enriched area, hydrocarbon analyses point to active biodegradation, particularly of the n-alkane fraction. This degradation is accompanied by severe oxygen depletion in sediments within 250 m of the platform. However, while there is a clear correlation between high hydrocarbon concentrations and biological effects, this does not necessarily imply a toxic effect since the faunal response is consistent with organic enrichment and not direct toxicity.

A recent report (IOE, 1985a) has indicated that a bacterial isolate from oil-based cuttings was twice as efficient at utilizing diesel than it was at utilizing a low toxicity base oil. This is probably a reflection of the diversity of potential carbon sources provided by the more complex diesel and may reflect co-oxidation mechanisms (e.g., oxidation only in the presence of other hydrocarbon or carbohydrate substrates). This may in turn, lead to slower weathering rates of low toxicity oil from cuttings and an increase in the potential for tainting of ground fish.

The final report of a United Kingdom study of the biodegradation of oil adhering to cuttings has now been released (IOE, 1985b). The study was designed to provide information on the normal degradation rates of oil in cuttings in a simulated sea bottom environment (running sea water tanks) and in enclosed 2 m diameter sea bed cylinders (approximately 25 m below sea surface in an enclosed sea loch) and to determine whether stimulated rates of biodegradation of the oil on cuttings could be achieved by addition of nutrients or bacteria acclimated to hydrocarbons. Samples of diesel oil-based mud (DBM) cuttings and low toxicity oil-based mud (LTM) cuttings were used for the experiments; running sea water DBM leaching experiments were carried out over 22 months while running sea water LTM experiments and sea bed cylinder experiments were carried out over 19 months.

Cores collected from the running sea water tanks were sectioned and analyzed by infra-red (IR) spectrometry. IR results from heavily loaded (2.5 - 7.5 cm thickness of cuttings) tanks were inconsistent, with only small, if any losses of oil from the surface (0 - 2 cm) layers of the cuttings. It was concluded that during the period of investigation, oil may have been supplied from deeper within the cuttings layer, thus maintaining an approximately constant oil level in the surface (0 - 2 cm) layers. No noticeable increase in hydrocarbon loss was noticed in the tanks containing nitrogen/phosphorus supplement, suggesting that at the level used (1% w/w) the supplement was not sufficient to establish a more abundant growth of microbial organisms in/on the treated cuttings. Results from lightly loaded (0.5 cm thickness of cuttings) tanks showed losses of 25 - 40% of oil from surface layers. Biodegradation of the hydrocarbons in the surface layers of the cuttings was observed and all tanks showed the formation of reducing conditions. It was concluded that it may be the depth of cuttings rather than the levels of oil associated with them that were primarily responsible for inducing reducing conditions. Retort analysis of the original cuttings used in the running sea water tanks and those cuttings sampled in March 1985 indicated losses of oil from surface layers of approximately 10% in the heavily loaded tanks and approximately

30% in the lightly loaded tanks. This again suggested that there was a supply of oil to the 0 - 2 cm upper layer of the cuttings from within the cuttings pile in deep layers of cuttings.

Visual inspections at the end of the experiment of the running sea water tank system indicated that surficial oil was still present in the heavily loaded tanks with LTM cuttings. The water in the heavily loaded tanks with DBM cuttings contained several floating clumps of a white microbial mat and the surface of the cuttings was completely covered in a white layer, or 'skin', of this mat. In the tanks with a light loading of LTM cuttings no surficial oil was present, nor was there any indication of the white microbial mat. In the lightly loaded tanks with DBM cuttings there were further indications that the cuttings were beginning to break down into smaller particles. Small patches of the microbial mat were found in both the tanks with a light loading of DBM cuttings (IOE, 1985b).

The two large seabed cylinders (2 m diameter) were dosed with 200 kg each of DBM and LTM cuttings. After an initial increase in oil concentrations of surface (0 - 2 cm) layers of the cuttings in the seabed cylinders, oil levels gradually decreased during the period of investigation. For the LTM cuttings an approximate 40% loss of oil from the surface layer (0 - 2 cm) took place during 9 months, while for the corresponding DBM cuttings the loss was approximately 15%. There appeared to be a slow upward movement of oil from deeper layers within the cuttings piles to the surface layers. Measurements of the ratios of $n\text{-}C_{17}$:pristane and $n\text{-}C_{18}$:phytane (DBM cuttings) and also $n\text{-}C_{15}$:farnesane and $n\text{-}C_{15}$:$i\text{-}C_{16}$ (LTM cuttings) indicated that some degradation of oil in these surface layers (0 - 2 cm) of cuttings was taking place alongside the physical removal by bottom currents. There was a marked increase (130 - 150%) in water content of the cuttings at 6 - 8 cm depth during the 19 month study, indicating a possible supply of oxygen and nutrients to this depth in a cuttings pile. Gas chromatograms of the oil associated with both DBM and LTM cuttings at 6 - 8 cm depth showed evidence of biodegradation of long chain alkane materials (IOE, 1985b).

Trace metal analysis (profiles) of cuttings from the seabed cylinders indicated that upper sections in the DBM cuttings were moderately enriched in iron (Fe) and manganese (Mn). Enrichment of barium (Ba), copper (Cu),

zinc (Zn) and manganese (Mn) was also found in upper sections of the LTM cuttings. The levels of most trace metals in the core sections related closely to the concentrations of Fe and Mn, illustrating the influence that hydrous oxides and hydroxides have on trace metal distributions in the cuttings and marine sediments (IOE, 1985b).

Nuclear magnetic resonance (NMR) analysis of the hydrocarbons associated with surface layers (0 - 2 cm) of the DBM and LTM cuttings in the seabed cylinders indicated that there was an appreciable decrease (approximately 15%) in straight chain alkane material associated with the DBM cuttings over the first 15 months of the experiment. For the corresponding LTM cuttings the decrease in straight chain alkane material was appreciably smaller (approximately 2%) (IOE, 1985b).

Results from a series of continuous culture vessel studies indicated that there was strong evidence for the presence of oil-degrading micro-organisms being present naturally in discharged cuttings. 'Seeding' of cuttings with bacteria was considered to be neither necessary nor desirable (IOE, 1985b).

Preliminary results of an exposure study in Canada of clams and sand dollars to oiled cuttings resulting from the use of a high aromatic base oil (Environmental Protection Service, 1985, Osborne, 1985, pers. comm.) also contained observations of the amount of oil released from the cuttings. The size and duration of the oil slick on each experimental tank varied with the well depth that the cuttings were collected from, and hence presumably with the formation composition. Heavy oil slicks were observed in the three tanks (containing cuttings from three different formation depths) for durations of 0, 6 and 13 days. Light oil slicks were observed for the rest of the time in the three tanks until the end of the 32 day experiment. The rate of release of oil from oiled cuttings thus appears to be highly variable and presumably very dependent on the formation type.

In the United Kingdom, Davies et al. (1984b) studied the effects of high aromatic OBM on fish trawled from stations close to and distant from

drilling platforms. The levels of hepatic aryl hydrocarbon hydroxylase (AHH) were determined in three species of bottom fish (cod, haddock and whiting). The data for cod and haddock showed significantly higher levels of AHH in the livers of fish caught close to drilling platforms than those caught in areas away from oil activity, while whiting showed no such differences. These data were concluded to be the first indications that the oil in sediments around platforms may be biochemically available to fish.

In Canada, a number of studies have been performed concerning the effects of oil-based drilling mud cuttings on fish. Addison et al. (1984) observed no toxic effects of low toxicity oil based cuttings on winter flounder over a 24-day test period. Sub-lethal assays of these flounder based on mixed function oxidase (MFO) measurements showed no induction of MFO enzymes nor of the cytochromes associated with them. Even in the "worst case" scenario of prolonged static exposures, no untoward lethal or sublethal effects were noted on the winter flounder, a species which shows MFO induction in the presence of other hydrocarbons.

Also on the basis of mixed function oxidase studies in fish, Payne et al. (1985) concluded that any potential for MFO induction by hydrocarbon contaminated cuttings would likely be reduced by substitution of low-aromatic base oils for diesel. They also comment that different classes of aromatic compounds appear to affect the fish differently, pointing out the difficulty of trying to deduce any sub-lethal effects, such as MFO enzyme induction, on the basis of total aromatic content.

2.4 EFFECTS OF MARINE DISCHARGES IN THE ARCTIC

There is at present no information available on the effects of OBM-contaminated cuttings discharged to an Arctic marine environment, although a current ESRF study at two offshore well-sites in the Beaufort Sea is addressing, in part, this data gap.

In many respects, the behaviour of the oiled cuttings in the shallow Beaufort Sea can be expected to parallel both situations found at Sable Island. Cuttings discharged during open water will be well mixed (dispersed and/or buried) by summer storms (similar to the shallow site) and the cuttings pile will be scoured by ice flows during periods of summer ice movement and during freeze-up. Cuttings discharged through the ice after freeze-up can be expected to settle directly around the discharge point (similar to the deep water site) because of the low currents usually prevalent during this time. As the ice cover breaks up, however, considerable shallow water scouring and dispersion of the cuttings pile is likely.

3.0 OIL LEACHING EXPERIMENTS

3.1 DESCRIPTION OF THE SET-UP OF THE EXPERIMENT

The objectives of this experiment were to perform laboratory studies to determine (a) the approximate rates and durations of release of oil from contaminated oil-based mud drilling cuttings and, (b) the potential formation of a surface crust on an oil contaminated drilling cuttings pile. Experiments were to be conducted in a static environment and in a wave environment typical of Beaufort Sea drilling locations.

The experimental facility was constructed in an unheated portable trailer on the foreshore of Patricia Bay (near Sidney, B.C.), across the road from the Dobrocky Seatech Ltd. facilities. The detailed experimental set-up is described in Section 5.1 and diagrammed in Figures 3.1 and 3.2.

Seawater was supplied to the trailer by a polyethylene intake line (76 m long and 3 cm diameter) that had the intake positioned 2 m below lower low water and 1 m off the bottom. The seawater was pumped into a 130 L constant head reservoir. The reservoir supplied water to the flow-through system through a supply line to the cooling tank. This line was connected to a 7.6 m length of cleaned copper cooling coil which was placed on the bottom of the ice bath between the two test tanks. The line then branched and cooled inlet water was piped into the two tanks; flow rates were controlled using ball valves and a small pump and were adjusted to replace the water in the test tanks every ten to twelve hours. The water level in the test tanks was controlled by the level of the outlet. Water flowing out of the tanks was passed through an oil-absorbing filter of polyurethane foam absorbant before discharge.

The three tanks were constructed out of 3/4 in. plywood and sealed with polyurethane resin and epoxy paint. The outer tank was filled with ice to serve as a cooling bath and was insulated on the top and sides. The two

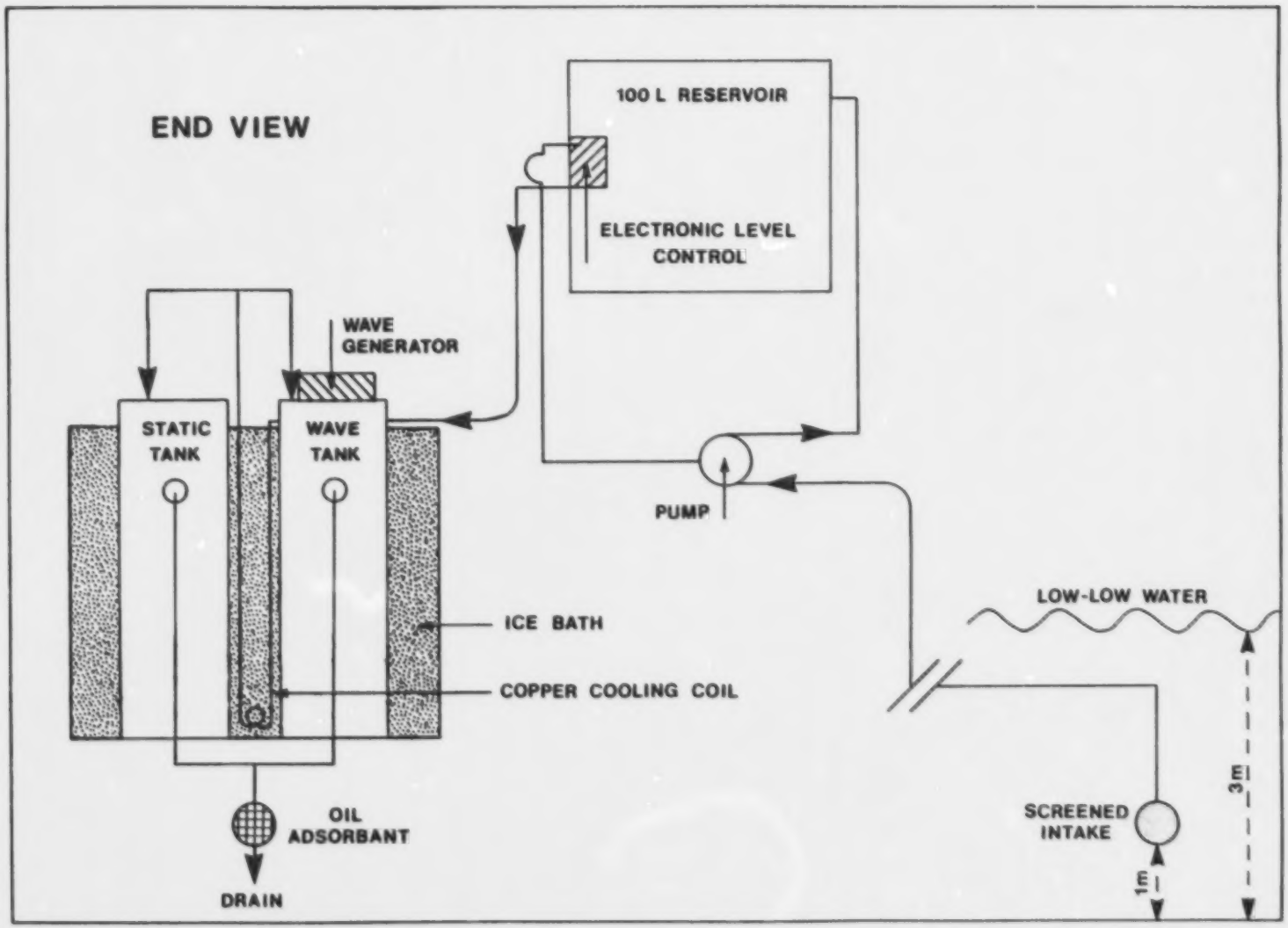


Figure 3.1 Overview of the experimental set-up.

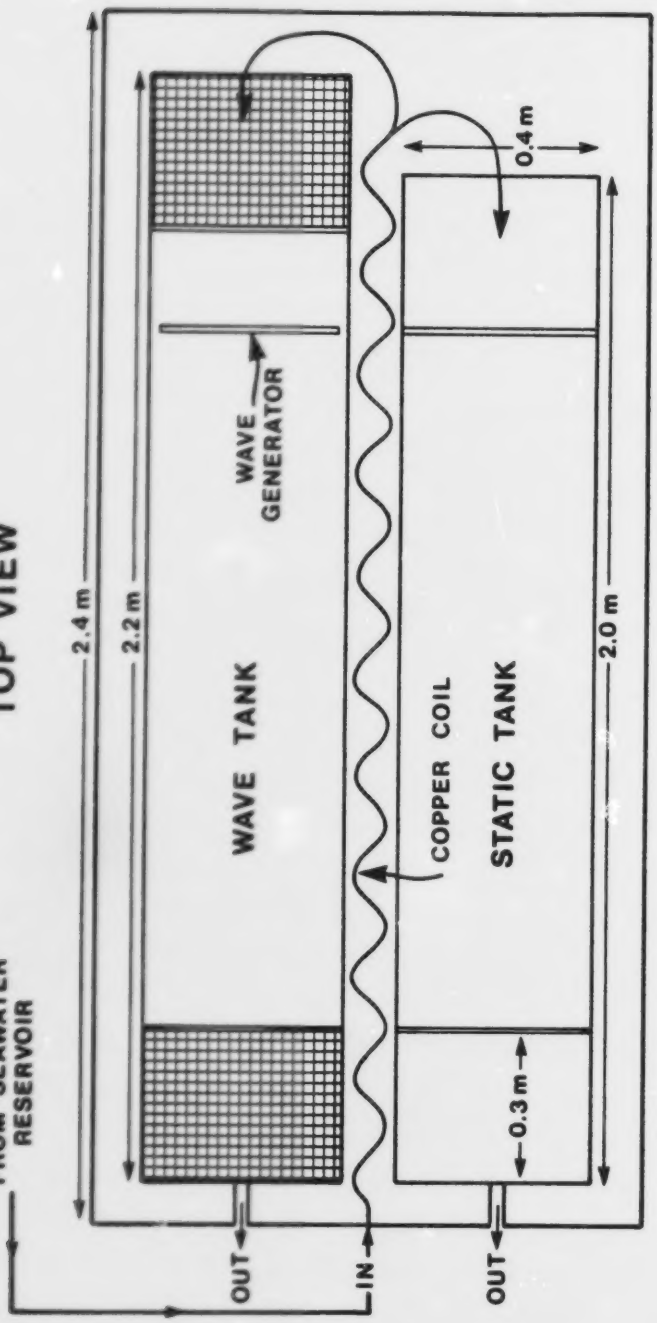


Figure 3.2 Top view of the experimental tanks.

test tanks (static and wave) were cooled by immersing in the ice bath. Additional cooling was provided by the inlet water which was precooled in the copper cooling coil at the bottom of the ice bath. Ice was purchased from a commercial supplier and stored in two large chest freezers until use. Since the experiment was run during the winter months, ice usage was relatively low except during periods of unusually warm weather.

One test tank had a wave regime and the other (the static tank) had a near laminar flow regime. The wave generator was constructed out of two 1/8 in. aluminum plates held 2.5 cm apart and powered using a small electric motor geared down using toothed gears and chain. Only 1.5 cm of space was left between the two tank walls and the aluminum wave generator plate. At the opposite end of the tank a wave damper made out of a sloped stack of acrylic egg crates with plastic vials behind it eliminated most of the wave reflections (see Section 3.4.2).

Five 20 L plastic pails of oily drilling mud cuttings, containing a total of about 80 L, were collected by INAC personnel at the Adgo G-24 wellsite and shipped to the Dobrocky Seatech Ltd. facilities in Sidney, B.C. A new cement mixer was used for mixing the oiled cuttings; oily residues remaining from manufacturing or shipping were removed by wiping down the inside with acetone soaked paper towels. Initially about 30-40 L of oiled cuttings were added to the mixer (this was its practical capacity) and well mixed. A portion of this material was then removed and replaced by new cuttings. This procedure was repeated numerous times over a three hour period until all of the oiled cuttings had passed through the mixer many times. At this point the oiled cuttings were transferred to the experiment site and the cuttings material was added to each tank, ensuring that the same volume of oiled cuttings was added to both tanks.

3.2 REFINEMENT OF THE SAMPLING DESIGN BASED ON THE RESULTS OF THE LITERATURE SURVEY

The initial sampling schedule proposed was planned with an exponential sampling period in mind (i.e., sampling on days 0, 1, 3, 6, 12, 24 and 48). This sampling period was based on the expectation that there would be an

initial wash out of oil (and possibly cuttings material) over the first week or so, particularly from the wave tank and then very little change after that. The exponential sampling scheme proposed would have been ideal to characterize this occurrence.

However, the literature review (Section 2.0 with particular reference to Section 2.3) indicated that this initial wash out of oil would likely be confined to "free or unbound" oil that floated away from the oiled cuttings when water was added. It was indicated to be very unlikely that any wash out of material would extend to the actual oiled cuttings in the static situation; the literature provided no guidance to the behavior of the oiled cuttings under the influence of a wave regime. The specific pieces of information from the literature that were used to refine the sampling design were as follows:

1. It has been observed that direct leaching of oil from cuttings into sea water appears to be very slow (Engelhardt et al., 1983) with initial rates of 0.1% of total oil per day and total losses in the order of 1 - 4% of total oil over a "substantial period of time" being quoted;

2. Leaching rates of "oil from cuttings" (neither described) have been found to be approximately 1-2 g/m^3/day (Poley and Wilkinson, 1983; De Jong, 1983);

3. The initial large release of "unbound" oil from cuttings appears to take place when the cuttings come in contact with water and usually only lasts a day or so (IOE, 1985b; Gillam, 1986 pers. comm.); and,

4. A continual migration of oil upward from the bottom of the cuttings pile has been observed in other studies (IOE, 1985b). This oil will replace the oil leached out into the water column and may even produce an increase in the surface oil content of the cuttings.

The change of well site providing the oiled cuttings from Nipturk L-19A to Adgo G-24 also resulted in a change of base oil from the high aromatic (25-30%) DMO-75 oil to Vista ODC (formerly Conoco ODC) which has an

aromatic content of <1%. This meant that the aromatic fraction of the base oil was expected to play an insignificant role in the leaching experiment and an hierarchical analysis scheme was proposed, with the hydrocarbon levels being quantified by Infra-red (Conrad et al., 1984) and with gas chromatography (GC) being used to examine qualitative changes in the oil composition (Yunker and Drinnan, 1986). The result was a substantial increase in the number of hydrocarbon analyses that could be performed.

A calculation was then done of the number of samples required to detect the expected changes in oil concentration. Conrad et al. (1984) report that 10 IR analyses of one 400 mL drilling cuttings sample yielded a mean oil concentration of 8.99% wet weight with a standard deviation of 0.25%. This corresponds to a coefficient of variation of 2.78%; for this level of analytical uncertainty, the analysis of three cuttings samples should be able to provide sufficient precision to detect a difference in cuttings oil concentration of slightly more than 5% (Keith et al., 1983).

The surface area of the oiled cuttings beds in both the static and wave tanks was 0.52 m^2; assuming an active oil loss layer 1 cm deep, the active layer would then have a volume of 5.0 L. A loss of oil of 2 $g/m^2/d$ (Poley and Wilkinson, 1983) corresponds to the loss of 1 g of oil per day over the whole cuttings surface in the static tank or 0.17% of the total oil in the active layer per day (assuming 12% oil in the cuttings). This, in turn, corresponds to a loss of 8% of the surface oil over 48 days and the analysis of three static tank cuttings samples by IR at each sampling time should be sufficient to detect this change. Changes in cuttings oil concentration were expected to be greater and more rapid in the wave tank and hence three cuttings samples would also be sufficient to detect any change in that tank.

Since the expected initial large release of "unbound" oil from the cuttings was expected to happen almost immediately, extra water samples were taken to try to characterize this release. However the sampling of cuttings was distributed more evenly over the duration of the experiment in order to

better characterize the expected slow release of oil from the cuttings (Section 2.3). This resulted in samples being taken on days 0, 1, 2, 5, 8, 12, 19, 26, 36, 48 and 49.

3.3 DESCRIPTION OF SAMPLING METHODS AND OF SAMPLES COLLECTED

The detailed sample collection matrix is given in Table 3.1. The table includes the day of the experiment (relative to the first day as Day 0), the date, the size of each water sample, the sampling location for each cuttings sample and the dates of cone penetrometer measurements and of changes in the oil absorbant. An effort was made to oversample so that samples would be available to fill in any data gaps.

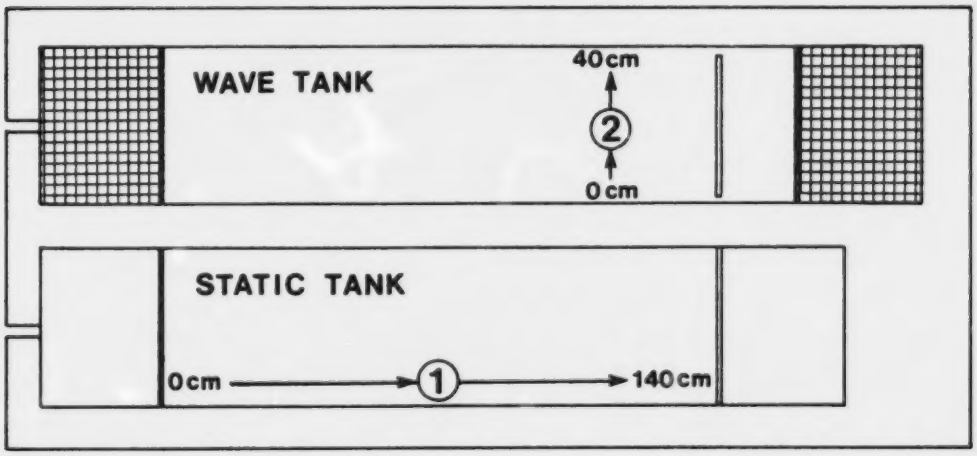
In the first few days of the experiment an attempt was made to collect cuttings samples by a number of coring procedures. Insertion of a full length core tube (i.e. longer than the water plus sediment depth) into the tanks and the use of a short (15 cm) core tube and the collection of a sample "by feel" met with little success (Section 5.1.5). An additional sampling device was constructed by cutting off about half of the side of a 1 L plastic bottle and fastening the remainder of the bottle (including the intact bottom) to a strip of plastic. This bottle was then lowered through the water to the surface of the cuttings and was then gently moved across the surface of the cuttings so that an intact sample was obtained of the top 1-2 cm of the sediment. With a little care, the sample was only collected from an area the size of the diameter of the bottle. It was then quite easy to lift the bottle back up to the surface, pour off the water and transfer the cuttings sample to a cleaned (oven baked at 400°C) bottle.

The latter procedure allowed the collection of an undisturbed sample of the cuttings surface from the bottom of each tank. Since this was the area of a cuttings pile that would actively leach oil into the water column, it was quite important that an undisturbed sample of this active layer be collected.

In most cases triplicate samples of the cuttings were collected on each sampling day. A random number generator was used to select locations for sampling in each tank and an effort was made not to sample any location twice. The area within 5 cm of the side of each tank was avoided to eliminate any influence of the tank walls on the samples. The position numbers in Table 3.1 were translated into sampling positions in the following manner (see diagram which follows):

- the first position number referred to a lengthwise measurement in each tank from the end of the cuttings bed that was opposite the wave generator; and,

- the second position number referred to a widthwise measurement in each tank starting from the edge of the tank closest to the center of the cooling bath.



Outlet water samples were obtained from the surface runoff outlet from the wave and static tanks by removing a replacable plug in each outlet line and collecting a 2-4 L sample. Since water flowed out of the tanks through these overflow ports, this meant that the sample collected would be taken from the surface water of each tank. Water samples were also collected

Table 3.1 Detailed Sample Collection Matrix.

Day	Date	Water Intake Sample	Water Outlet Sample		Cuttings Sample		Cone Penetrometer		Change Oil Absorbant
			Static	Wave	Static	Wave	Static	Wave	
					Six samples of cuttings after mixing				
-5	Jan. 24								
-1	Jan. 28				Surface Skim	Surface Skim			
0	Jan. 29		2L	2L					
1	Jan. 30		2L	2L	50 x 10 cm	20 x 10 cm	X	X	
2	Jan. 31		2L	2L					
5	Feb. 3		4L	4L	40 x 20 cm 25 x 25 cm 110 x 10 cm	25 x 10 cm 75 x 10 cm 125 x 10 cm			X
8	Feb. 6	4L	4L	4L	80 x 15 cm 110 x 10 cm 60 x 20 cm	105 x 30 cm 80 x 25 cm 130 x 25 cm	X	X	
12	Feb. 10	4L	4L	4L	30 x 30 cm 10 x 30 cm 30 x 10 cm	115 x 15 cm 60 x 30 cm 50 x 10 cm	X	X	X
19	Feb. 17	4L	4L	4L	115 x 15 cm 60 x 30 cm 50 x 10 cm	65 x 20 cm 85 x 10 cm 115 x 20 cm	X	X	
26	Feb. 24	4L	4L	4L	20 x 15 cm 120 x 20 cm 30 x 20 cm	35 x 10 cm 10 x 15 cm 130 x 10 cm	X	X	X
36	Mar. 6	4L	4L	4L	80 x 30 cm 125 x 25 cm 60 x 30 cm	90 x 15 cm 105 x 30 cm 115 x 15 cm	X	X	
48	Mar. 18	4L	4L	4L	60 x 10 cm 25 x 10 cm 95 x 20 cm	40 x 30 cm 80 x 25 cm 100 x 10 cm	X	X	
49	Mar. 19		4L Surface + Subsurface	4L Surface + Subsurface	120 x 25 cm 35 x 20 cm 10 x 20 cm	110 x 10 cm 15 x 10 cm 60 x 15 cm	X	X	X
					Surface + Subsurface	Surface + Subsurface			

from the seawater intake (at the point that the inlet line split before going into the two test tanks) so that the hydrocarbon background level could be established. At the end of the experiment (Day 49) surface and subsurface water samples were collected from inside each tank. After draining the tanks, Day 49 surface and subsurface cuttings samples were also taken. Oven-baked (400°C) bottles were used for the collection of all samples.

3.4 INCORPORATION OF WAVE MIXING INTO THE EXPERIMENTAL DESIGN

3.4.1 Description of the Model Wave Obtained

In order to model typical Beaufort Sea waves in the laboratory, we sought to maintain the same value for wave particle velocity at the cuttings surface and the same ratio of the water depth to the wave length; i.e.,

$$(U_o)_m = (U_o)_p \tag{1}$$

and $$h_m/L_m = h_p/L_p \tag{2}$$

where U_o is the amplitude of the oscillatory wave particle velocities, h is the still water depth and L is the wave length. The subscripts m and p refer to the model and prototype (nature) systems respectively.

It can be shown that at the bottom of the water column:

$$U_o = \frac{agT}{L} \frac{1}{\cosh(2\pi h/L)} \tag{3}$$

where a is the wave amplitude (one-half the wave height), g is the acceleration of gravity and T is the wave period.

The wave length can be expressed in terms of the period through the dispersion relation:

$$L = \frac{gT^2}{2\pi} \tanh \frac{2\pi h}{L} \tag{4}$$

Substituting (4) into (3), we get:

$$U_o = \frac{2\pi a}{T} \frac{1}{\sinh (2\pi h/L)} \qquad (5)$$

Equation (5) shows that for a given value of h/L, the bottom wave particle velocity amplitude is proportional to a/T, i.e.,

$$h_m/L_m = h_p/L_p \qquad (5)$$

implied that $a_m/T_m = a_p/T_p$ (6)

Information on the size of a typical Beaufort Sea summer wave (0.75 m high, 5-7 s period) was obtained from Esso Resources Ltd. (Spedding, 1985 pers. comm.). We then strove to model a non-directional monochromatric wave in 10 m of water with the following characteristics:

$T_p = 6$ s $\qquad h_p = 10$ m

$a_p = 0.375$ m $\qquad L_p = 48$ m

$h_p/L_p = 0.208$

However laboratory limitations including:

1) a significant reflected wave due to incomplete wave damping;
2) restrictions on the amplitude of the wave generator; and,
3) restrictions of the period of the waves generated,

necessitated using the model described by the following values:

$T_m = 1.0$ s $\qquad h_m = 0.5$ m

$a_m = 0.035$ m $\qquad L_m = 1.5$ m

$h_m/L_m = 0.333$

Since $h_m/L_m \neq h_p/L_p$, equation (6) does not apply. Using equation (5):

$$(U_o)_m = \frac{2\pi(0.035)}{1.0} \quad \frac{1}{\frac{\sinh 2\pi(0.5)}{1.5}} = 0.055 \text{ m s}^{-1}$$

$$(U_o)_p = \frac{2\pi(0.375)}{6} \quad \frac{1}{\frac{\sinh 2\pi(10)}{48}} = 0.229 \text{ m s}^{-1}$$

Our model velocities were therefore one-quarter of the prototype velocities. This would correspond to a Beaufort Sea wave of 0.75 m height and 6 s period (the design wave) in 23 m of water.

3.4.2. Incident and Reflected Components of the Model Wave

Since we were unable to completely dampen the waves created by the wave generator in the experimental tank, this resulted in wave energy being reflected back toward the wave generating paddle. The resulting wave field was a superposition of a pure progressive wave travelling away from the generator and a pure standing wave fixed in space. Figure 3.3a shows the variation of wave amplitude along the wave tank; note that the wave amplitude would vanish at the "pseudo-nodes" if there were no purely progressive wave component. In order to keep the wave contained in the tank, we could not further increase the wave amplitude.

The distribution of wave amplitude can be used to compute the amplitude of the incident and reflected waves which interfere to form a standing and a progressive wave. At the antinode, the amplitude is equal to the sum of the incident and reflected wave amplitudes:

$$I + R = 5 \text{ cm} \qquad (7)$$

and at the "pseudo-nodes" the amplitude is equal to the difference in the incident and reflected wave amplitudes:

$$I - R = 2 \text{ cm} \qquad (8)$$

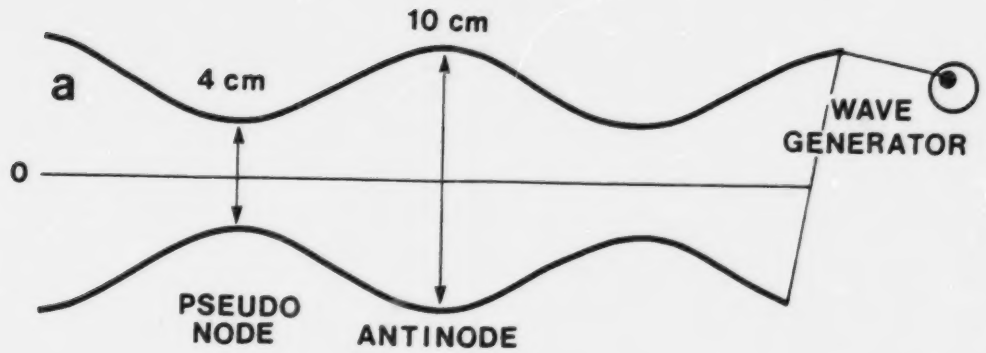


Figure 3.3a Distribution of wave amplitude along the wave tank due to the super-position of a purely progressive and a purely standing wave.

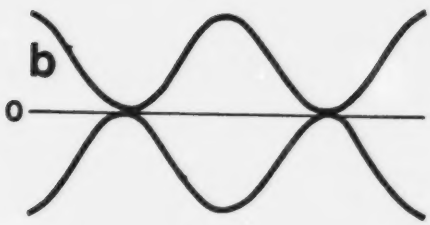


Figure 3.3b Standing wave of amplitude S (3 cm).

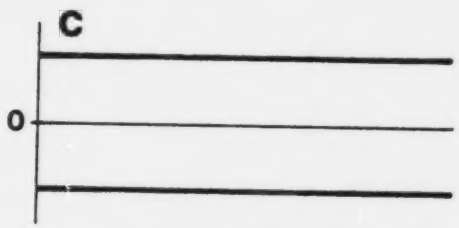


Figure 3.3c Progressive wave of amplitude P (2 cm).

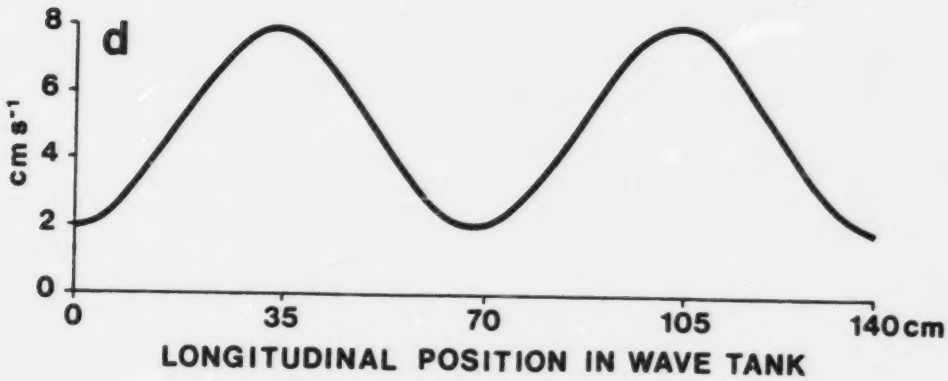


Figure 3.3d Horizontal distribution of the amplitude of the wave particle velocities due to the super-position of the purely progressive and purely standing wave components.

Solving equations (7) and (8):

$I = 3.5$ cm

$R = 1.5$ cm

Hence the reflected wave amplitude is just over 40% of the incident wave amplitude and the reflected wave energy is:

$$1.5^2/3.5^2 = 0.18$$

or 18% of the incident wave energy. This means that we succeeded in dissipating 82% of the wave energy.

It should be noted that having the reflected wave equal to about one-half of the incident wave provided a good model of the situation obtained windward of an artificial island or solid drilling structure.

The incident and reflected waves formed a standing wave of amplitude 3 cm and a purely progressive wave of amplitude 2 cm. These are shown in Figures 3.3b and c. At the antinode, the progressive wave of amplitude P, reinforced the standing wave of amplitude S. Since S was a function of position along the tank, the wave particle velocities also varied along the tank. The velocities due to the standing wave were highest under the pseudo nodes, while the progressive wave velocity amplitude was constant along the tank. The horizontal distribution of the amplitude of the wave particle velocities is shown in Figure 3.3d.

4.0 RESULTS AND DISCUSSION

The experimental set-up and sampling design and schedule were described in the previous section. The cuttings in the static tank were undisturbed by any turbulence or wave action and the relatively low water replacement rates (1 L/min or one water change every 10-12 h) ensured that water flow through the static tank was very close to laminar. Size limitations on the height of the tanks and the wave damper provided an upper limit on the wave amplitude. As a result, the wave damper used was only 82% efficient and the wave particle velocities that we were able to achieve were only one-quarter of the desired values. However, the reflected wave had approximately one-half the amplitude of the incident wave and this was felt to provide a good model of the situation windward of an artifical island or solid drilling structure. The water depth modeled (23 m) was also typical of the water depths at many of the Beaufort Sea drilling sites.

4.1 PHYSICAL OBSERVATIONS

An oil-based drilling mud using Vista ODC (formerly Conoco ODC) base oil was used at the Adgo G-24 well site in the depth range of 475 m to 3087 m. The formations drilled were unconsolidated with a high mud content and a highly variable texture (ranging from muds to pebbles). Drilling commenced October 1, 1985 and finished January 13, 1986. During this time the cuttings were stored in plastic lined sea cans on the island; temperatures ranged from about +5°C to -45°C during this period. Cuttings samples were collected the week that drilling finished and received in good order at the Dobrocky Seatech Ltd. facilities on January 21, 1986.

The physical description of the oiled cuttings in the static and wave tanks at the beginning and end of the experiments is given in Table 4.1. Note that the major source of disturbance in both the wave and static tanks appeared to be from the sampling and the cuttings resistance (cone

Table 4.1 Description of the Oiled Cuttings in the Experimental Enclosures

CUTTINGS DEPTH	STATIC TANK	WAVE TANK
A. Before Experiment (Day 0)		
All depths (0-7 cm)	Oiled cuttings were loose and unconsolidated, with oil on the surface. After fill-up the water took on a dark brown colour with visible oil on the water surface.	Oiled cuttings were loose and unconsolidated, with oil on the surface. After fill-up and wave start up the water formed a brown emulsion.
B. After Experiment (Day 49)		
Surface (0-2 cm)	The top 2-3 cm of cuttings were brown/grey and unconsolidated. The cuttings were oily with a visible oil film and spots of oil.	The top 1-2 cm of cuttings were grey/black and relatively loose with a "jello-like" consistancy. The cuttings were watery and showed only a little visible oil.
Bottom (2-7 cm)	The cuttings material to the bottom (7 cm) was more cohesive and consolidated than the top material but much more similar to the surface material than in the wave tank. There was no "pavement" formation.	The cuttings were dense and very cohesive; they were still oily and almost "water free". The bottom material was hard and compact and could be described as "bottom pavement".

The major source of disturbance in <u>both</u> tanks appeared to be from the sampling and cuttings resistance (cone penetrometer) measurements.

penetrometer) measurements. A visible oil film remained on the surface of the cuttings in the static tank throughout the experiment. The visibility in the wave tank remained too poor to clearly observe the cuttings, however, at the end of the experiment the surface cuttings showed only a trace of visible oil.

At the start of the experiment, large amounts of free oil were observed floating on the water surface (a dark brown color) in the static tank, but only a little oil was observed on the water surface in the wave tank. This difference was attributed to the amount of "free" oil present in each tank at the point when the water was added. When the wave generator was first started the water formed a brown emulsion, however, the wave generator had to be left off overnight on the first day (Section 5.1.4). After two hours of operation on the second day, the water was oily but not emulsified, and at this time one could barely see the bottom. This poor visibility appeared to be due to fine particulate material in suspension and not due to oil emulsion. After this time the wave generator was only off for short periods of time either for sampling or minor repairs.

One of the most unexpected physical observations was the formation of a subsurface "bottom pavement" in the wave tank. The use of a sediment cone penetrometer was added to the experiment at the last minute, in an attempt to measure the oiled cuttings resistance. However, the initial very unconsolidated nature of the cuttings necessitated a more than 30 fold increase in the load bearing area of the penetrometer (to the point that the penetrometer would almost "float" on the cuttings; see Section 5.1.6) with the result that cuttings resistance measurements only applied to the cuttings surface. As a result, any hardening or consolidation of the cuttings in the subsurface layers of the cuttings bed could not be detected with this technique.

Since all of the available cuttings material was used for the leaching experiments, additional cuttings material was not available for calibration of the cone penetrometer voltage to the cuttings depth penetration. Note

that the modifications to the penetrometer were not performed until after the cuttings were in the tanks. In addition, since the penetrometer was large (over 20 cm diameter) in comparison to the total surface area of each cuttings bed, multiple measurements could not be made without excessively disturbing the cuttings surface, and potentially jeopardizing the rest of the leaching experiment. Hence no precision information was available for any of the penetrometer measurements. This lack of information was not entirely fortuitous. The modifications to the cone penetrometer were so extensive (in its final form it was no longer even a cone), that the measurements were considered to be of a qualitative nature, and hence were given secondary importance relative to the leaching experiments. It is likely that a much deeper cuttings bed and an extensively modified penetrometer design would be necessary for rigorous measurements of the oiled cuttings resistance.

As can be seen from the (qualitative) resistance measurements (Table 4.2), there was a gradual decrease in cuttings surface resistance in the static tank and a gradual increase in resistance in the wave tank. The formation of a hard and compact "bottom pavement" below a relatively loose layer of watery cuttings was not detected until the cuttings were examined at the end of the experiment. It should be noted that the hard (plywood) tank bottom could have accelerated the consolidation of the subsurface cuttings by providing a rigid surface against which the waves could compact the cuttings. It is possible that the cuttings would not consolidate as quickly or to the same degree if they were placed on a softer bottom.

Temperature profiles for the static and wave tanks are given in Figure 4.1. The mean temperature in both the static and wave tanks was 5°C ($s = 2°C$). Additional insulation was added to the tops of the tanks on Day 6 and this provided an immediate reduction in temperature. In general the temperatures in both tanks paralleled each other and were relatively stable unless the ambient temperature climbed above 10°C (as it did after Day 30) or dropped below 2°C (Days 16-23). The experiment was originally scheduled for the months of December and January when the mean temperatures

Table 4.2 Sediment Penetrometer Readings for the Wave and Static Tanks

Date	Day	Static Tank (Volts)	Wave Tank (Volts)
Jan. 30	1	0.052	0.036
Feb. 06	8	0.101	0.056
Feb. 10	12	0.092	0.065
Feb. 17	19	0.095	0.076
Feb. 24	26	0.075	0.075
Mar. 06	36	0.065	0.090
Mar. 18	48	0.043	0.101

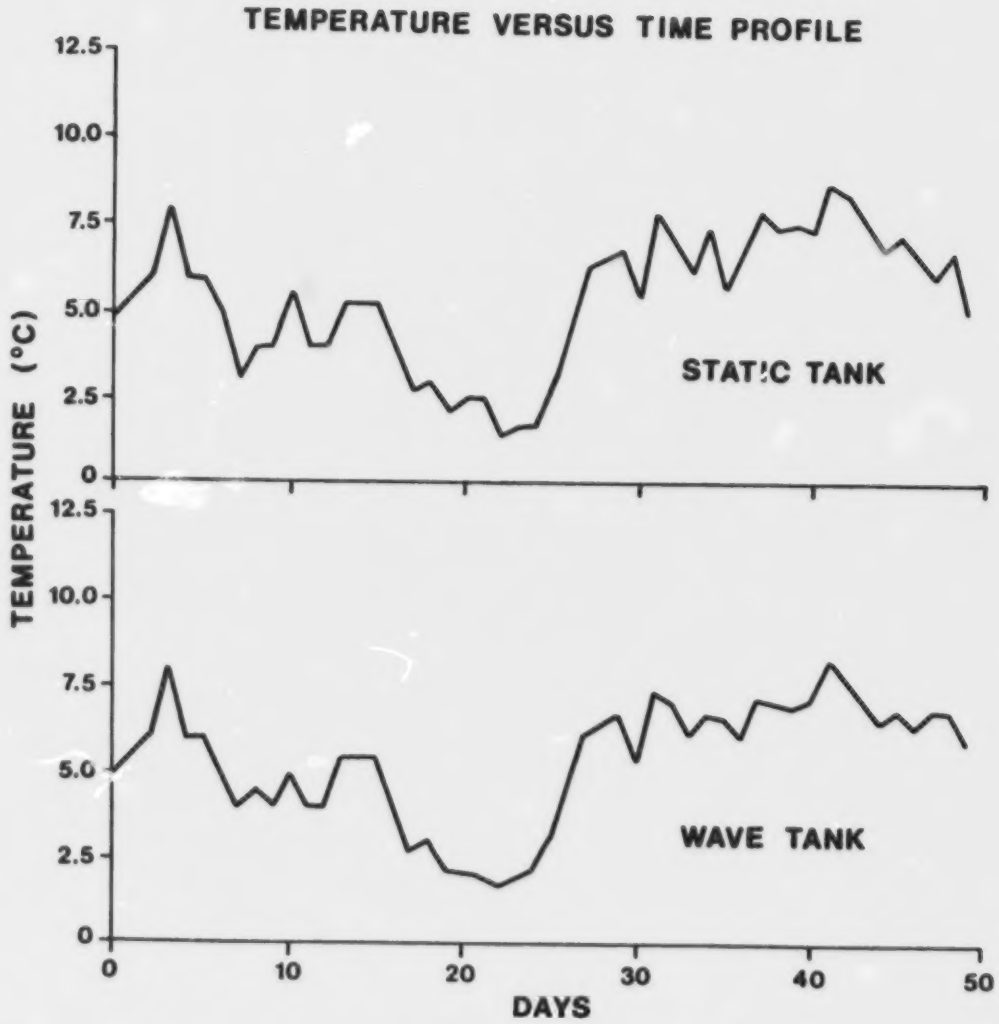


Figure 4.1 Temperature profiles for the static and wave tanks.

in Victoria are usually below 5°C. When the start of the experiment was delayed until the end of January, neither time nor resources were available for extensive modifications to the cooling system. Note that the designed cooling system proved adequate for the expected low temperature regime but was not able to cope with the warmer temperatures encountered during March. A more elaborate cooling system would be necessary for experiments planned during this time.

4.2 OIL CONTENT OF CUTTINGS AND WATER SAMPLES

The analytical methods used to measure the oil content of the seawater and cuttings are described in detail in Section 5.2. Pre-experiment concentrations of oil on the cuttings measured by the operator (retort method) and measured in samples of homogenized cuttings sampled on Day -5 (IR method) are given in Table 4.3. The later concentrations were used as a baseline for the interpretation of the experimental results.

The homogenized cuttings samples (from Day -5) also provided a good estimate of the precision of the extraction method. A coefficient of variation of 9.6% was obtained for these five analyses. The other Quality Assurance/Quality Control technique used was verification (using reagent blanks) that the reagents and extraction procedure made a negligible contribution to the oil concentrations measured in the samples.

The concentrations of oil on cuttings for the static tank and wave tank respectively are shown in Tables 4.4 and 4.5 and diagrammed in Figures 4.2 and 4.3. The concentrations of oil in water are given in Table 4.6. The inlet water did not contain detectable amounts of hydrocarbons by either IR or GC analysis techniques.

In the static tank, the cuttings surface oil concentrations showed an initial increase as oil floated to the top of the cuttings pile (the base oil is about 0.23 kg/L less dense than seawater) and then remained relatively constant throughout the experiment. The water samples showed an

Table 4.3 Pre-experiment Concentration of Oil on the Adgo G-24 Cuttings

A. Measured by the Operator (retort method)

Well Depth m	Oil Concentration mg/g
800	223 (shakers)
1100	177 (shakers), 141 (centrifuge)
2400	134 (shakers)

B. Samples of Homogenized Cuttings Sampled on Day -5 (IR method)

Subsample	Oil Concentration mg/g ash weight	$\bar{x} \pm s$
1	-	114 ± 11
2	113	
3	102	
4	131	
5	108	
6	118	

Table 4.4 Concentration of Oil on Cuttings in the Static Tank

Day	Subsample	Oil Concentration mg/g ash weight	$\bar{x} \pm s$
1	50 x 10	158	158
5	40 x 20	194	179 ± 15
	25 x 25	164	
	110 x 10	178*	
8	80 x 15	101*	117 ± 17
	110 x 10	134	
	60 x 20	116	
19	115 x 15	228	225 ± 3
	60 x 30	223	
	50 x 10	223	
26	20 x 15	182	189 ± 8
	120 x 20	187	
	30 x 20	197	
36	80 x 30	193	198 ± 7†
	125 x 25	47.8	
	60 x 30	203	
48	60 x 10	193	205 ± 32
	25 x 10	242	
	95 x 20	181	
49 Surface	120 x 25	174	178 ± 13
	35 x 20	168	
	10 x 20	193	
49 Subsurface	120 x 25	166	169 ± 7
	35 x 20	164	
	10 x 20	177	

* Value approximate.
† The low value (47.8) was omitted for this calculation.

Table 4.5 Concentration of Oil on Cuttings in the Wave Tank

Day	Subsample	Oil Concentration mg/g ash weight	$\bar{x} \pm s$
1	20 x 10	153	153
5	25 x 10	347	340 ± 71
	75 x 10	407	
	125 x 10	265	
8	105 x 30	148	120 ± 53
	80 x 25	206	
	130 x 25	253	
19	65 x 20	211	303 ± 100
	85 x 10	289	
	115 x 20	410	
26	35 x 10	514	521 ± 49
	10 x 15	475	
	130 x 10	573	
36	90 x 15	380	480 ± 111
	105 x 30	460	
	115 x 15	600	
48	40 x 30	183	228 ± 86
	80 x 25	174	
	100 x 10	328	
49 Surface	110 x 10	181	281 ± 95
	15 x 10	370	
	60 x 15	293	
49 Subsurface	110 x 10	49.9	57.7 ± 32.1
	15 x 10	30.2	
	60 x 15	93.0	

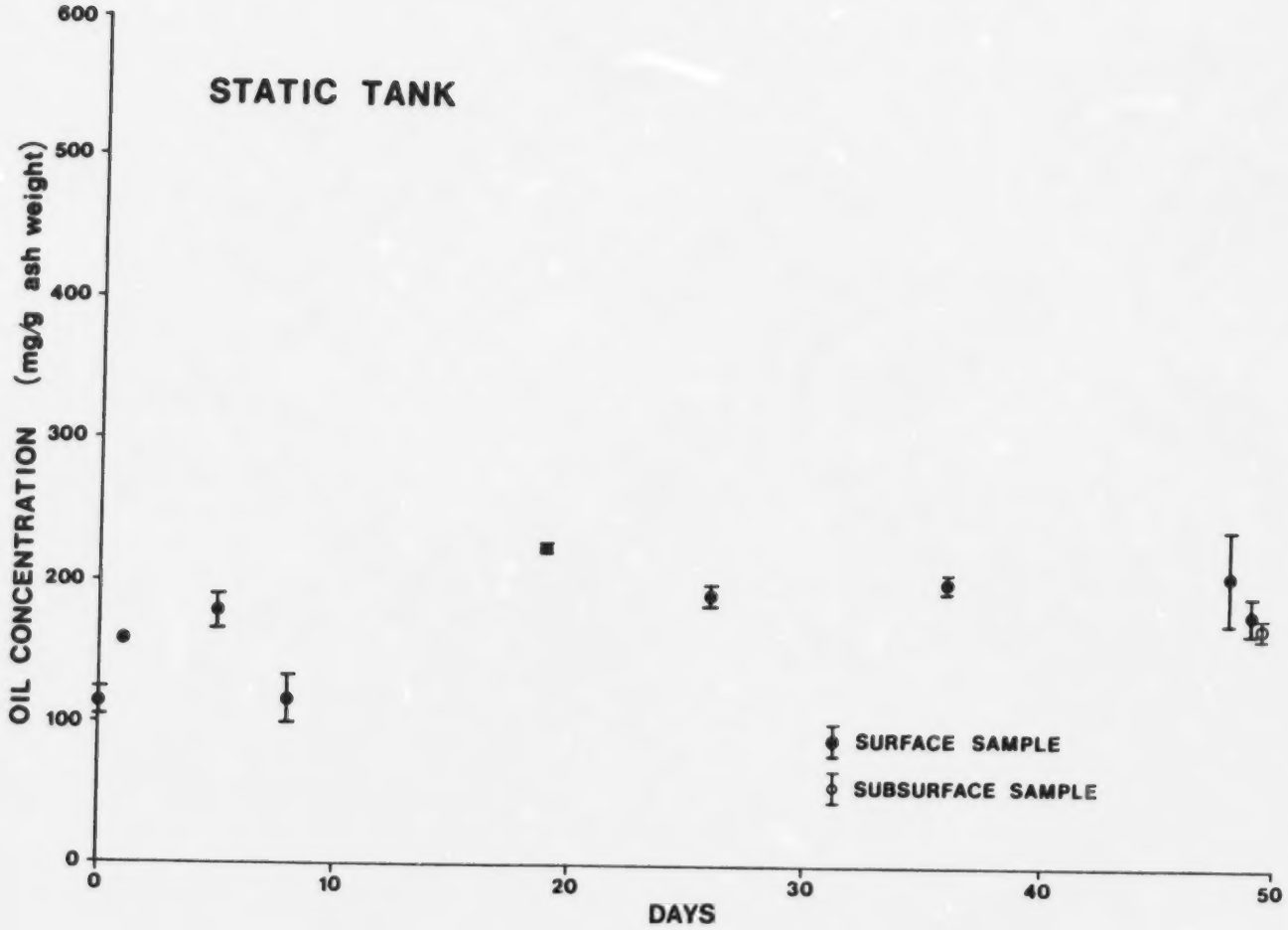


Figure 4.2 Concentrations of oil on cuttings for the static tank. Values given are the mean plus or minus the standard deviation.

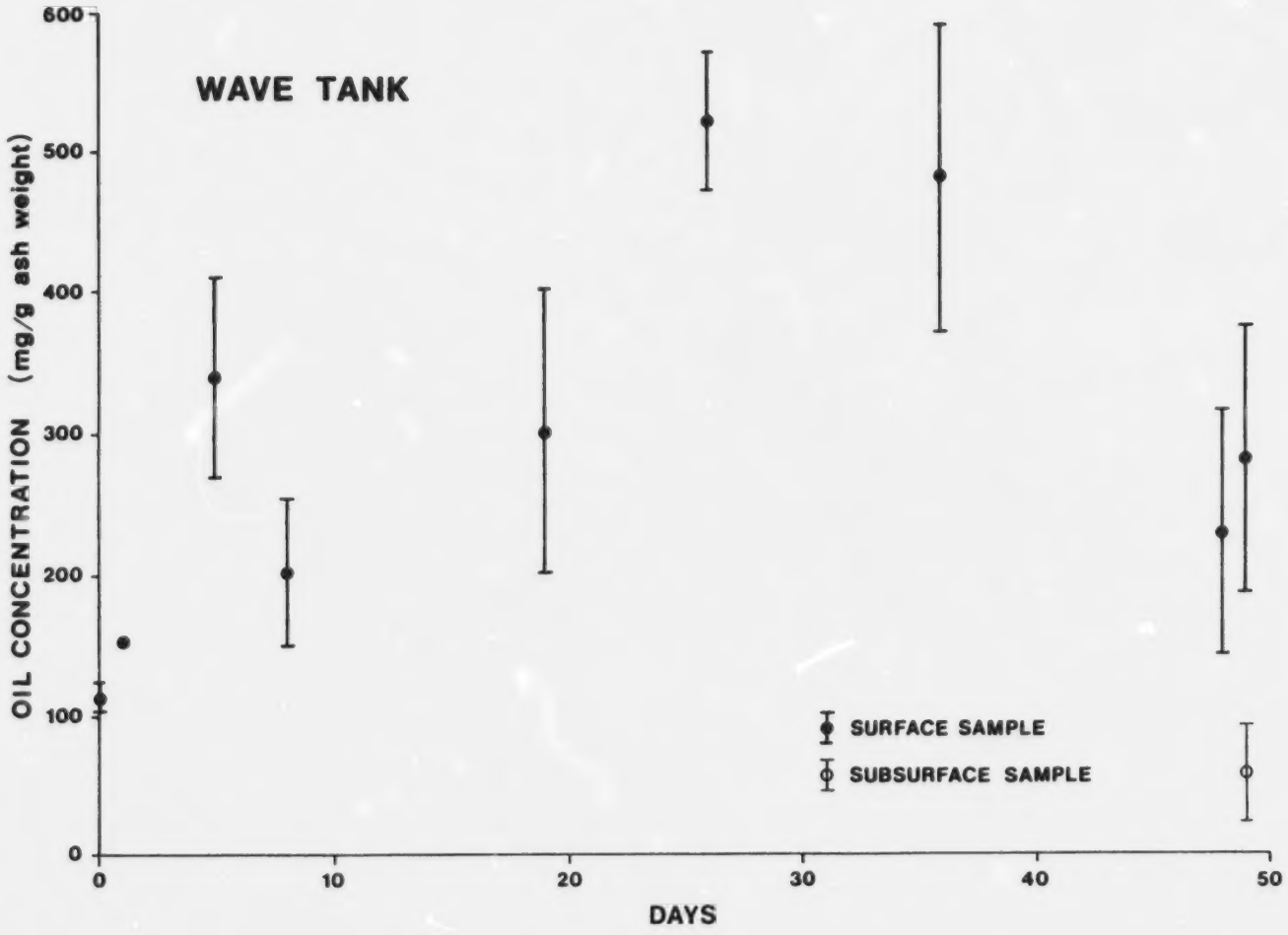


Figure 4.3 Concentrations of oil on cuttings for the wave tank. Values given are the mean plus or minus the standard deviation.

Table 4.6 Concentration of Oil in Water

Sample Type	Day			Oil Concentration mg/L
Inlet	8			<0.2
	26			<0.2
	48			<0.2
Static Tank	0			15,000
	1			92
	2			2.6
	5			<0.2
	8			3.8
	12			300
	19			1300
	26			3.9
	36			1.5
	48			16
	49	Surface	-1	540
			-2	170
		Subsurface	-1	<0.2
			-2	<0.2
Wave Tank	0			15
	1			1.1
	2			4.7
	5			3.4
	8			130
	12			0.3
	19			11
	26			8.5
	36			<0.2
	48			<0.2
	49	Surface	-1	<0.2
			-2	<0.2
		Subsurface	-1	<0.2
			-2	1.0

initial massive release of oil (with an oil in water concentration of 1.5% on Day 0) followed by a relatively steady low part per million oil level. Since the water samples were collected from the surface runoff from the tank, the amount of oil measured would be dominated by the number of surface oil drops that happened to be collected with the sample. This would explain why the Day 12 and Day 19 water samples were elevated.

On Day 49, surface water samples were collected in duplicate by partially immersing two 4 L bottles and collecting samples of the surface layer. Subsurface water samples were collected by completely immersing two closed bottles, removing the tops underwater and allowing the bottles to fill, and then recapping the bottles before bringing them back through the surface layer. These samples (Table 4.6) showed that the oil was present only in the surface layer of the water. Static tank cuttings samples collected on Day 49 showed no significant difference (alpha(2) = 0.05) in the oil content of the surface and subsurface samples (t-test; Natrella, 1966).

In the wave tank, the cuttings surface oil concentrations increased to a maximum of about 3.5 times the initial oil concentration at a point about half-way through the experiment and then decreased to a level just above the initial concentration. Throughout most of the experiment, cuttings surface oil concentrations were much greater in the wave tank than in the static tank. Surface water oil concentrations in the wave tank were however in general lower than in the static tank and fell below the limit of detection approximately half-way through the experiment. The large Day 0 difference between the surface oil concentrations measured in the static and wave tanks (Table 4.6) was attributed to substantial differences in the amount of "free" oil present in each tank at the point when the water was added.

On Day 49, surface and subsurface wave tank water samples showed in general no detectable oil. Wave tank cuttings samples collected on Day 49 showed a significant difference (alpha(2) = 0.05) in oil content between the surface and subsurface samples with the surface samples having significantly higher oil concentrations (t-test; Natrella, 1966).

The cuttings surface oil concentrations were tested further using a non-parametric two way analysis of variance (Zar, 1984). The hypotheses tested were:

H_o1: Cuttings surface oil concentrations were not affected by the presence of waves;

H_o2: Cuttings surface oil concentrations did not change with time during the experiment; and,

H_o3: There was no interaction between the presence of waves and the day of the experiment which affected the cuttings surface oil concentrations.

In order to provide sufficient replication for the test, surface oil concentrations for Days 5, 8, 19, 26, 36, 48 and 49 were used for both the wave and static tanks (Tables 4.4 and 4.5). The data were ranked as described by Zar (1984). The ranks were then summed for each cell and the rank sums were obtained for each level of each factor. The sums of squares of the ranks and the degrees of freedom were tabulated for calculation of the Kruskal-Wallis H statistic. If H exceeded the Chi-squared value for alpha = 0.05 and the available degrees of freedom, then the hypothesis was rejected.

H_o1 was rejected and H_o2 and H_o3 were accepted. We can conclude that the cuttings oil concentrations were significantly affected by the presence of waves. However on the average, when both tanks were considered together, the cuttings surface oil concentrations did not change with time during the experiment. Presumably the lack of change in the static tank has influenced the results of this test. Finally, we can conclude that the two major factors in the experiment (waves and time) did not act together to induce variation in the data set. If this hypothesis of no interaction between the major factors had been rejected it would have been an

indication that the experiment was improperly designed or conducted. Its acceptance is an indication that the two factors were independent and that the experiment has been properly conducted.

H_o2 was retested for the wave tank alone. Once again surface oil concentrations from Days 5 to 49 were used. The non-parametric Kruskal-Wallis analysis of variance was used (Zar, 1984) and the H statistic calculated. If H exceeded the Chi-squared value for alpha = 0.05 and the available degrees of freedom, then the hypothesis was rejected. This time H_o2 was rejected which indicated that the cuttings surface oil concentrations did change significantly with time during the experiment in the wave tank.

Since the wave in the wave tank was partially (18%) made up by a reflected wave, the wave particle velocities at the cuttings surface were not constant throughout the wave tank (Section 3.4.2 and Figure 3.3d). Accordingly, the surface oil concentrations were tested for linear correlations with the wave particle velocities at each sampling position (Zar, 1984). The surface oil concentrations for the entire experiment were less than 1% correlated to the wave particle velocity and the surface oil concentrations measured toward the end of the experiment (Days 36, 48 and 49) were only 3% correlated. In addition, neither correlation was significant even at a low probability level ($p < 0.50$). It was concluded that the differences in wave particle velocity did not have a significant effect on the experiment.

Since the surface oil concentrations in both tanks dropped significantly (alpha(1) = 0.05, t-test, Natrella, 1966) from Day 5 to Day 8 and since these decreases coincided with a decrease in temperature (Figures 4.1 - 4.3), possible linear correlations between the water temperature and the surface oil concentration were also investigated (Zar, 1984). The surface oil concentrations were much less than 1% correlated ($r^2 = 2.5 \times 10^{-5}$) with temperature in the static tank and just less then 1% correlated ($r^2 = 0.0076$) in the wave tank. Neither correlation was

significant, even at a low probability level ($p < 0.50$). While the change in temperature may have been an influencing factor in the change in surface oil concentrations between Days 5 and 8, the data available do not support the hypothesis that temperature has had a significant impact on the over all experiment. This conclusion must however be tempered by the realization that the leaching experiment was not designed to test this hypothesis.

To the best of our knowledge, experiments have not been done to test the effects of temperature (or salinity) on the leaching of oil from drilling cuttings. Since changes in temperature (and salinity) will effect the viscosity of seawater, any changes will have at least a small effect on a wave tank experiment. Similarily, hydrocarbons are in general more water soluble as the temperature is increased, but large temperature changes are required to have an appreciable effect, and the water solubilities are very low in any case. It is felt that any changes in temperature observed (or of salinity which might have occurred) during the experiment will have had a negligible effect on the experiment when compared to the profound effects of waves relative to a static exposure.

Similarily, the linear correlation between the surface oil concentrations and the sediment penetrometer voltages (Tables 4.2, 4.4 and 4.5) was also investigated (Zar 1984). The two data sets were less than 1% correlated in the static tank and 3.8% correlated in the wave tank. Neither correlation was significant at the usual levels tested ($p < 0.05$) although the correlations in the wave tank were just significant at $p = 0.05$. It can be concluded that there was no simple relationship between the surface oil concentrations and the surface resistance.

4.3 COMPOSITIONAL CHANGES IN THE BASE OIL DURING THE EXPERIMENT

4.3.1 Cuttings Samples

The GC trace for one of the samples of pre-experiment cuttings homogenate collected five days before the start of the experiment (Day -5) is shown in

Figure 4.4. The other sample analyzed by GC yielded identical results. Methods used for GC analysis are described in Section 5.2.4. On each GC figure shown in this section, the labels n-C8 to n-C18 indicate the retention times of the even numbered normal alkanes from octane to octadecane.

Note that at the beginning of the experiment, the base oil showed a symmetrical envelope of hydrocarbons ranging from nonane to hexadecane (n-C9 to n-C16) and a ratio of resolved peaks to the UCM (unresolved complex mixture) of about 3:1 (see Figure 4.4). Surface cuttings samples collected on Day 1 in both the static and wave tanks showed the same envelope and proportion of resolved peaks as the base oil at the beginning of the experiment (Figures 4.5 and 4.6). All of the GC traces run of static tank cuttings samples showed essentially the same trace as the pre-experiment sample (Figure 4.4) although there was some indication of loss of the n-C9 to n-C10 fraction in one of the Day 36 samples (Figure 4.7). The GC traces of surface and subsurface samples from the static tank on Day 49 are shown in Figures 4.8 and 4.9. The GC traces of static tank surface samples from Days 5, 8, 19, 26 and 48 are given in Appendix 1.

GC traces were run for all cuttings samples analyzed from the wave tank. Examples are given in Figures 4.10 - 4.15. All of the wave tank surface cuttings samples except two showed little or no change in the base oil composition, although some samples showed an indication of a minor reduction in the proportion of resolved peaks. For example the ratio of the resolved peaks to the UCM is about 2:1 for the 90 x 15 cm Day 36 sample (Figure 4.10), but the ratio is back up to 3:1 for the 15 x 10 cm Day 49 surface sample (Figure 4.12). The two surface samples which showed a marked change in the base oil composition were collected on Day 36 and Day 49 (Figures 4.11 and 4.14 respectively). In both of these samples, hydrocarbons have been lost from the envelope from the range of n-C9 to n-C11 but the ratio of resolved to UCM peaks has remained at about 3:1.

All three of the subsurface cuttings samples collected on Day 49 from the wave tank showed this loss of hydrocarbons (two of the three GC traces are

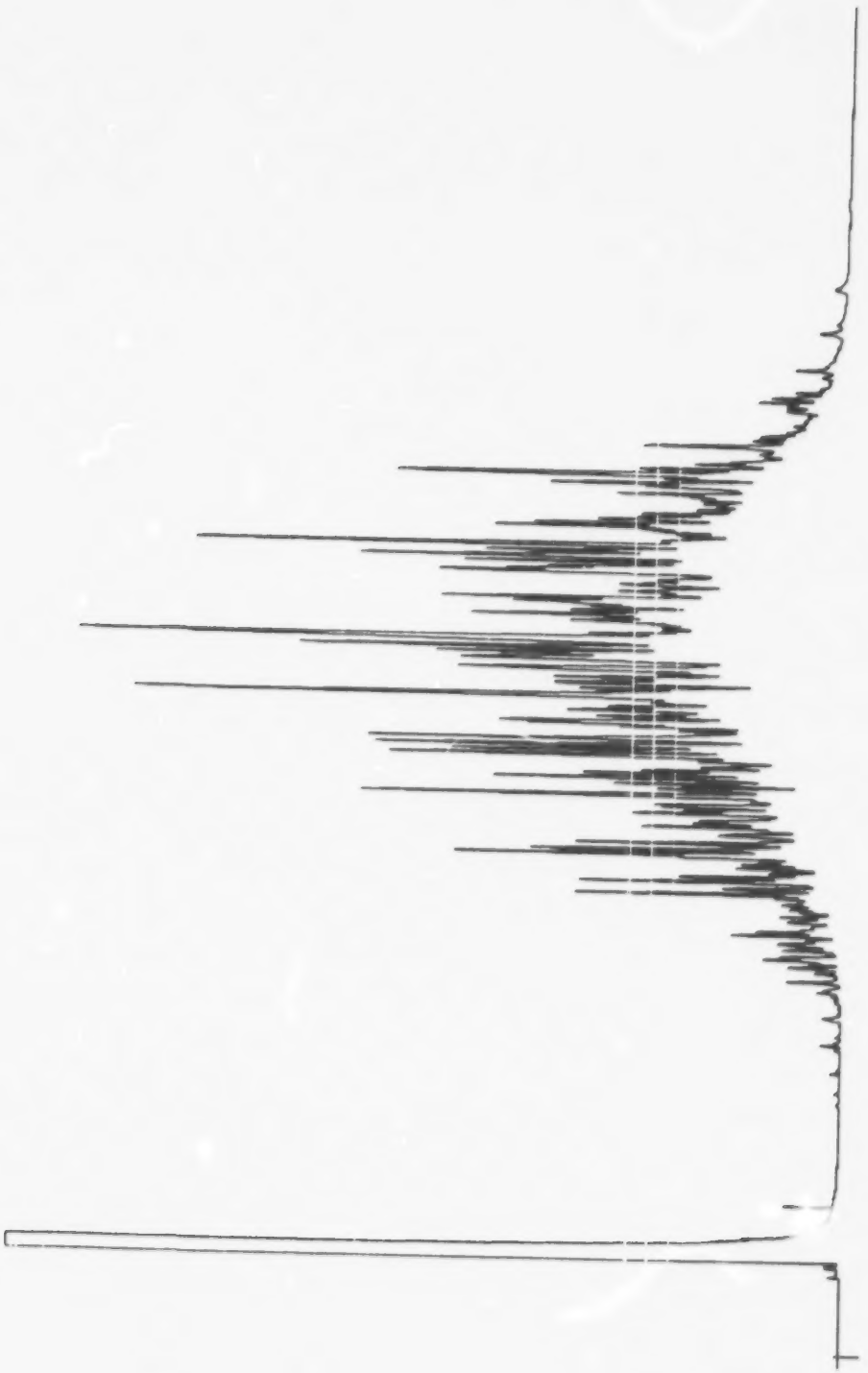


Figure 4.4 GC trace of pre-experiment cuttings. Homogenate sample number 6.

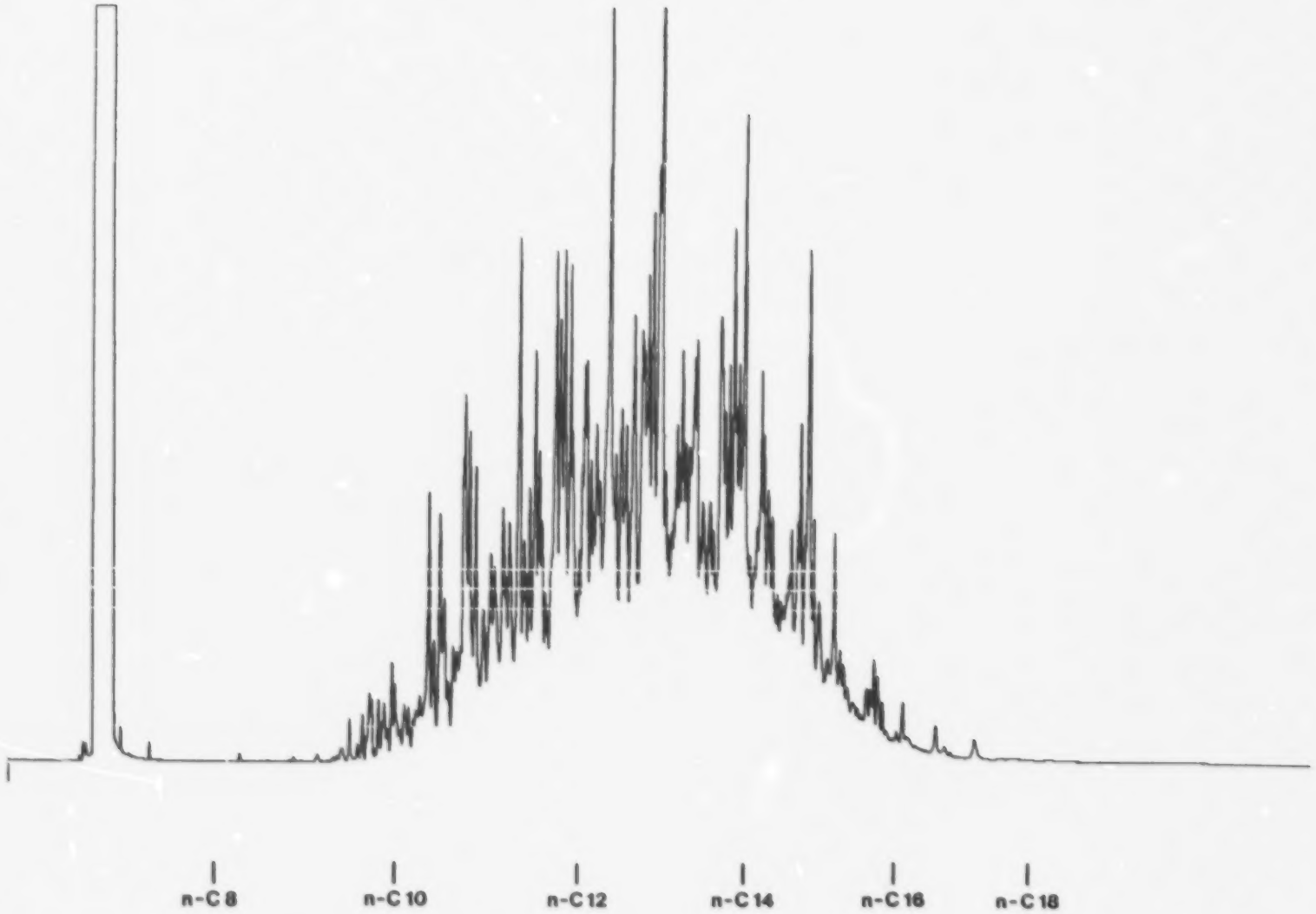


Figure 4.5 GC trace of the 50 x 10 cm surface sample of cuttings collected on Day 1 in the static tank.

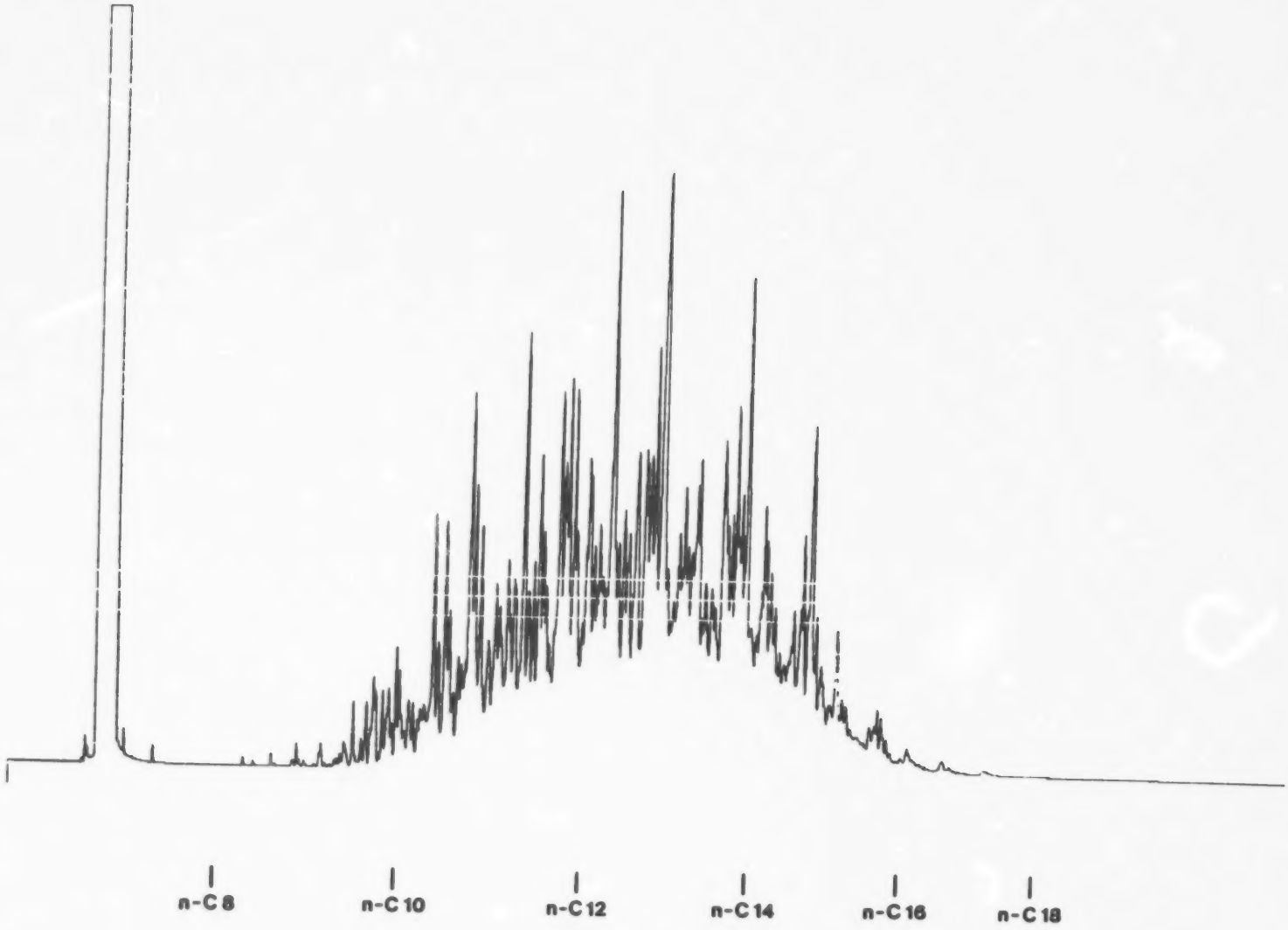


Figure 4.6 GC trace of the 20 x 10 cm surface sample of cuttings collected on Day 1 in the wave tank.

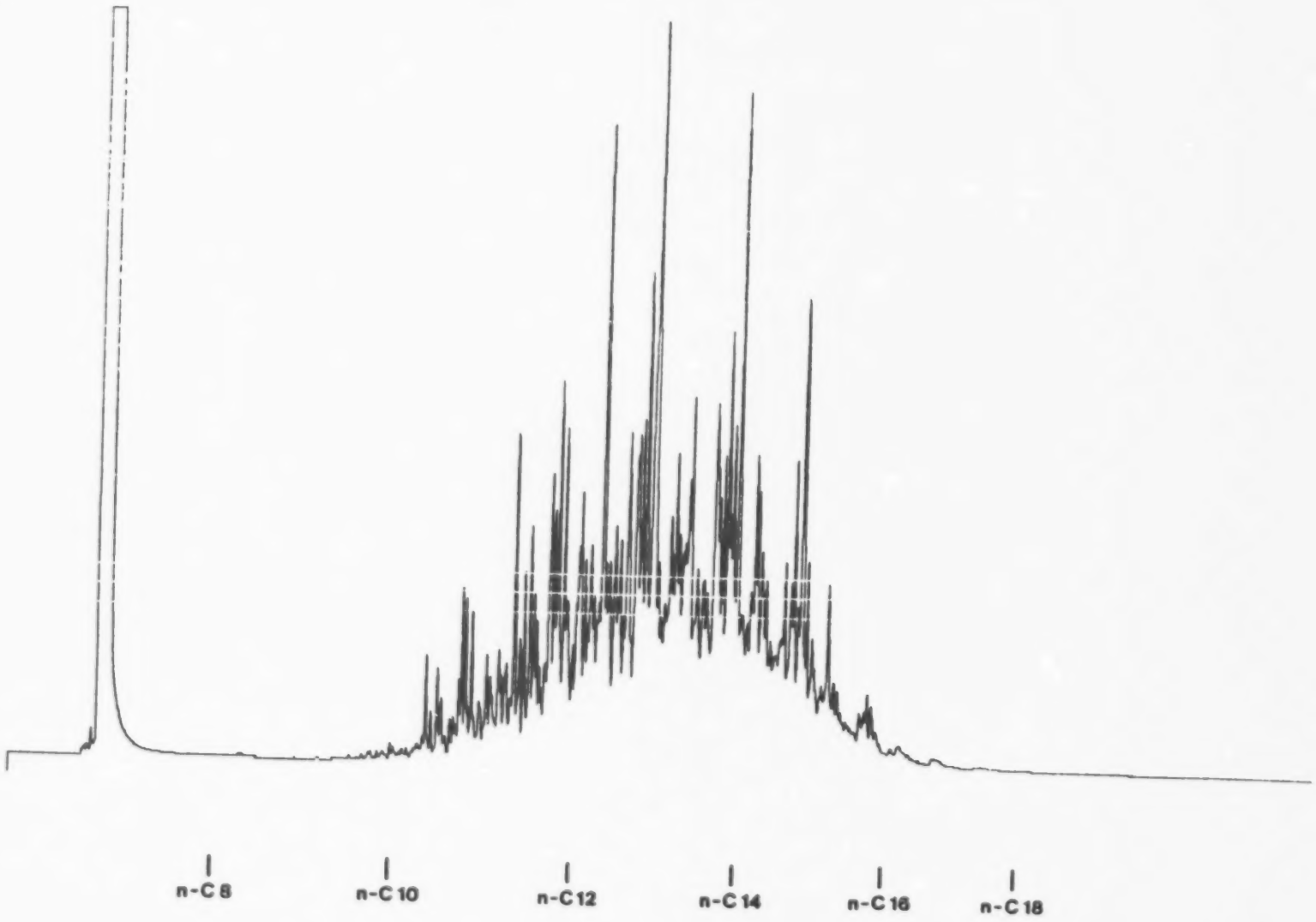


Figure 4.7 GC trace of the 60 x 30 cm surface sample of cuttings collected on Day 36 in the static tank.

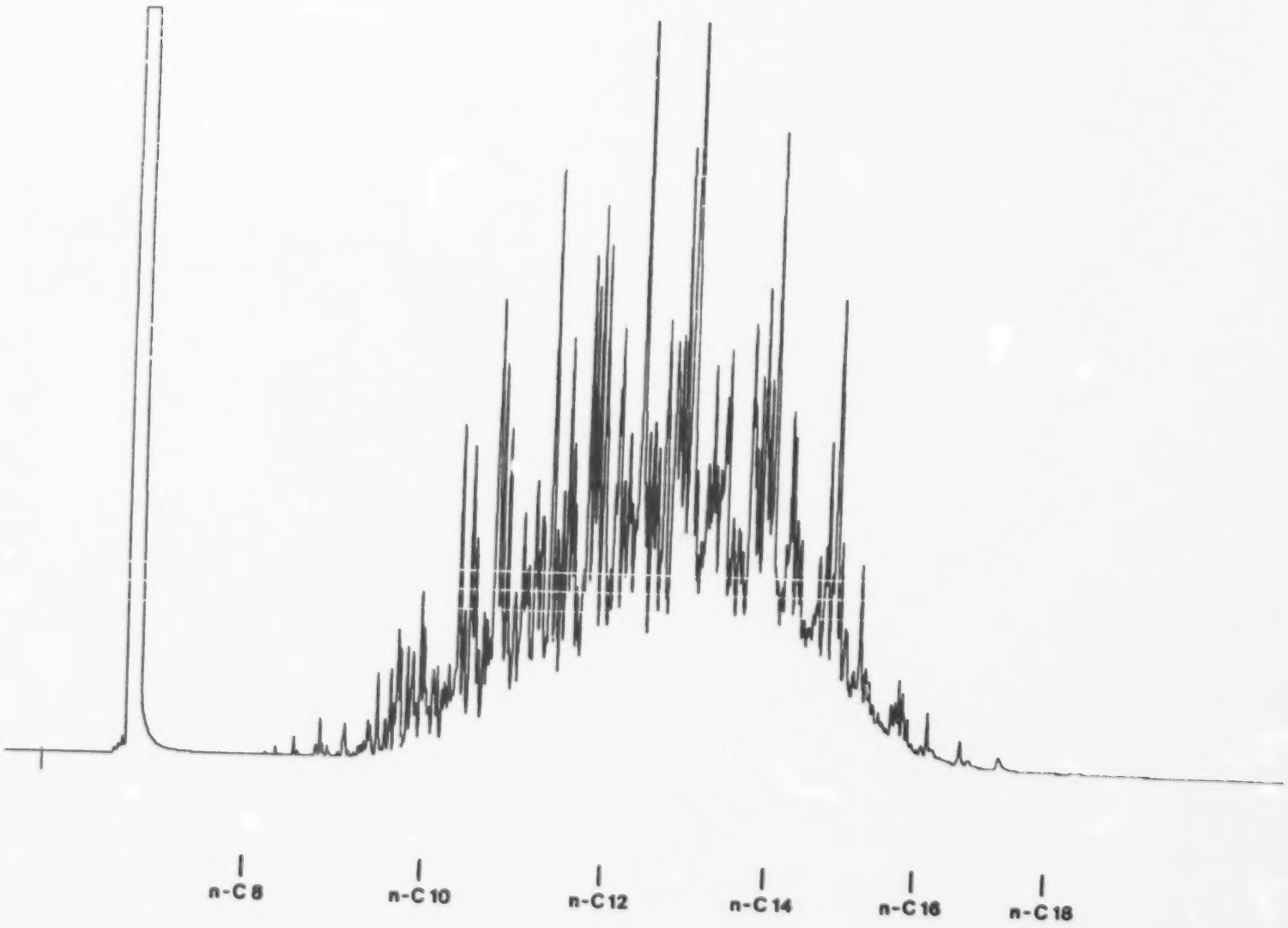


Figure 4.8 GC trace of the 35 x 20 cm surface sample of cuttings collected on Day 49 in the static tank.

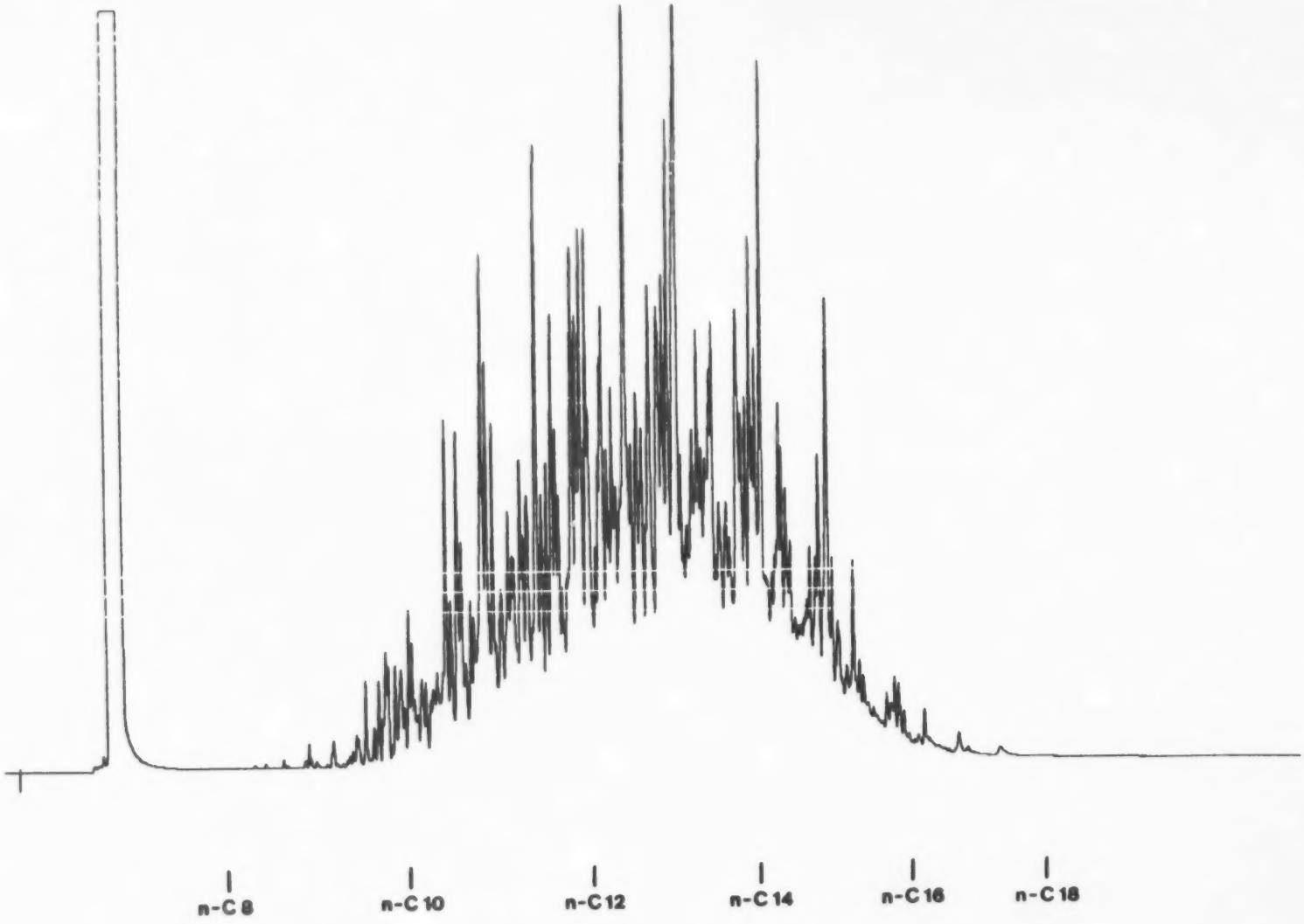


Figure 4.9 GC trace of the 35 x 20 cm subsurface sample of cuttings collected on Day 49 in the static tank.

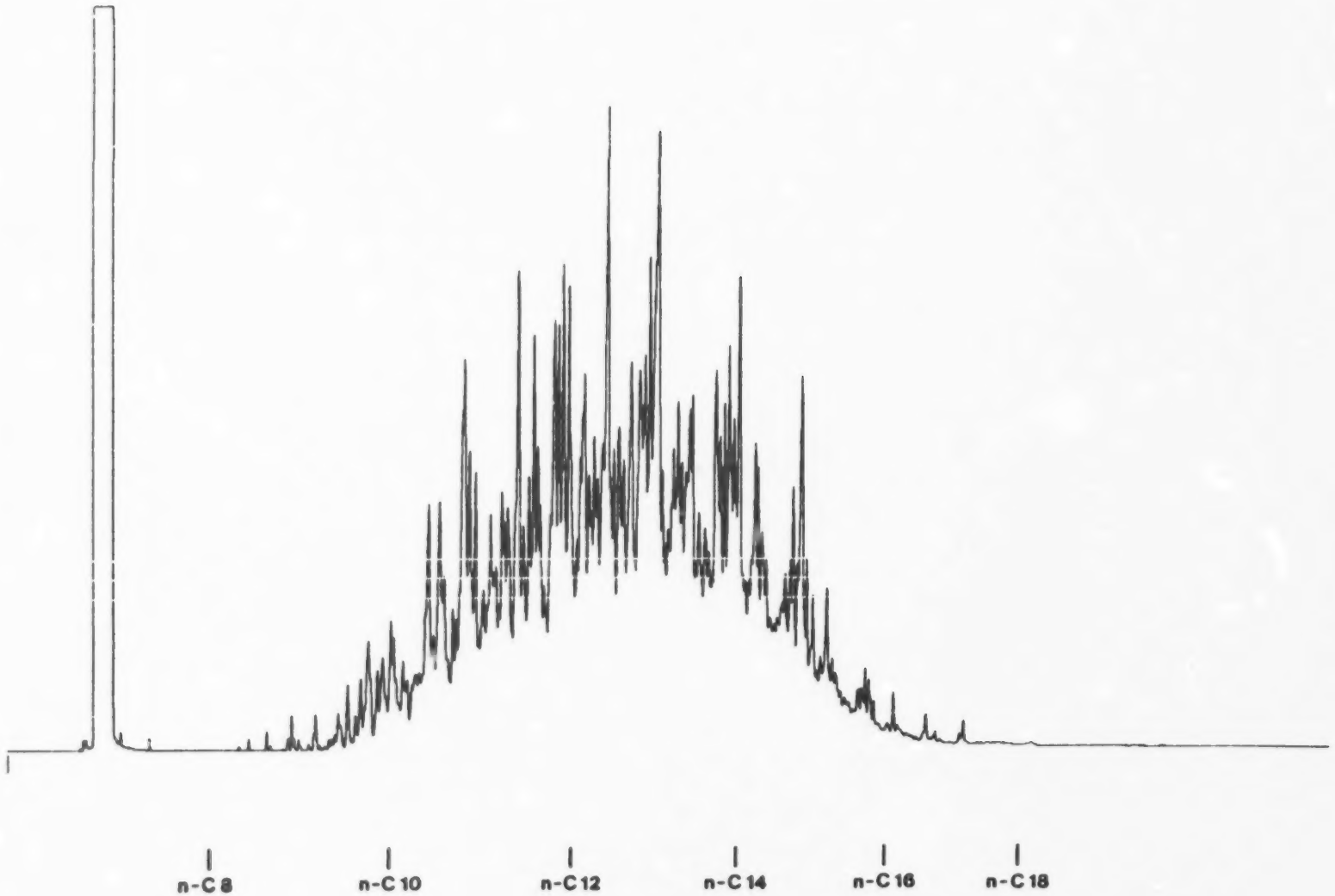


Figure 4.10 GC trace of the 90 x 15 cm surface sample of cuttings collected on Day 36 in the wave tank.

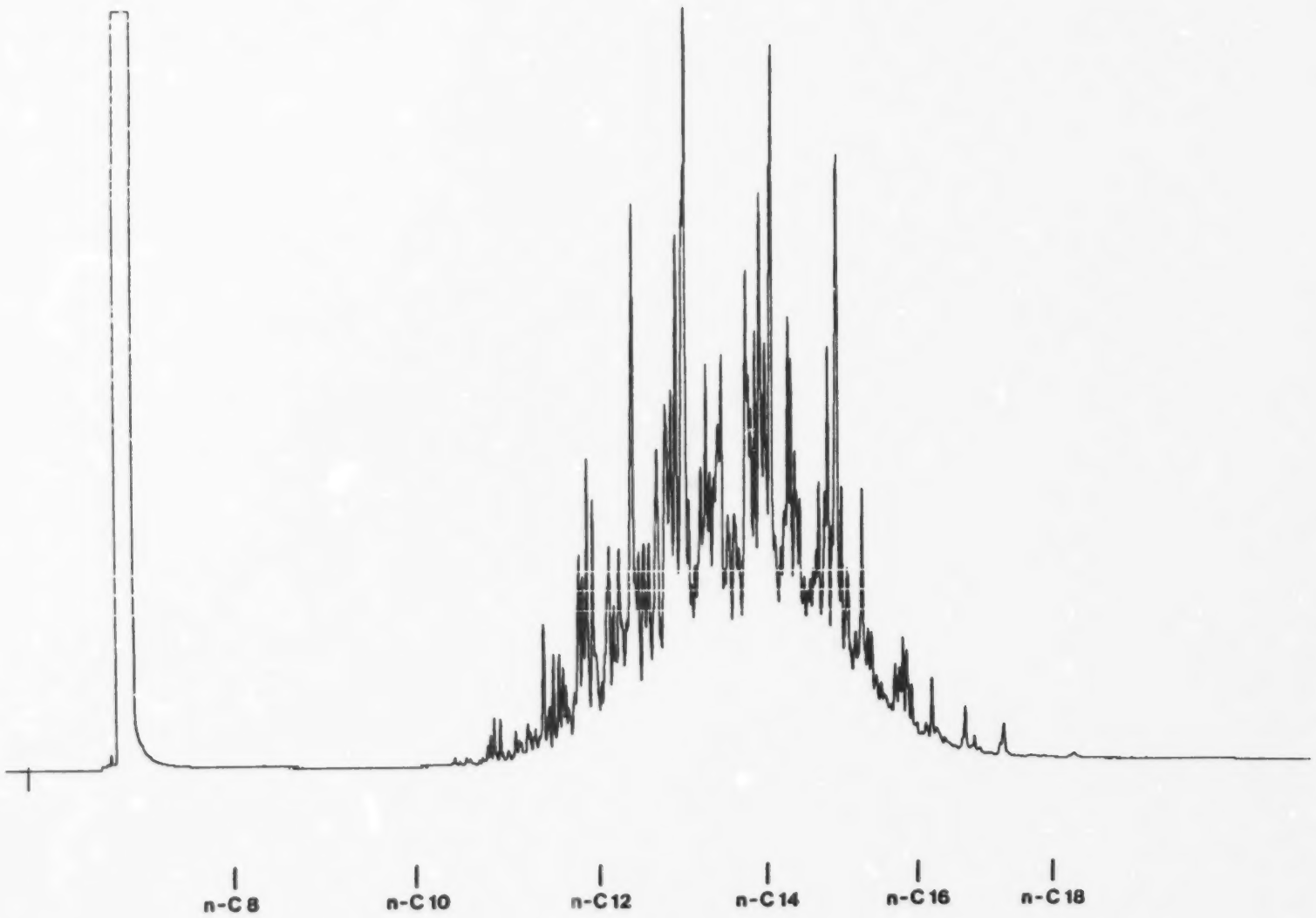


Figure 4.11 GC trace of the 115 x 15 cm surface sample of cuttings collected on Day 36 in the wave tank.

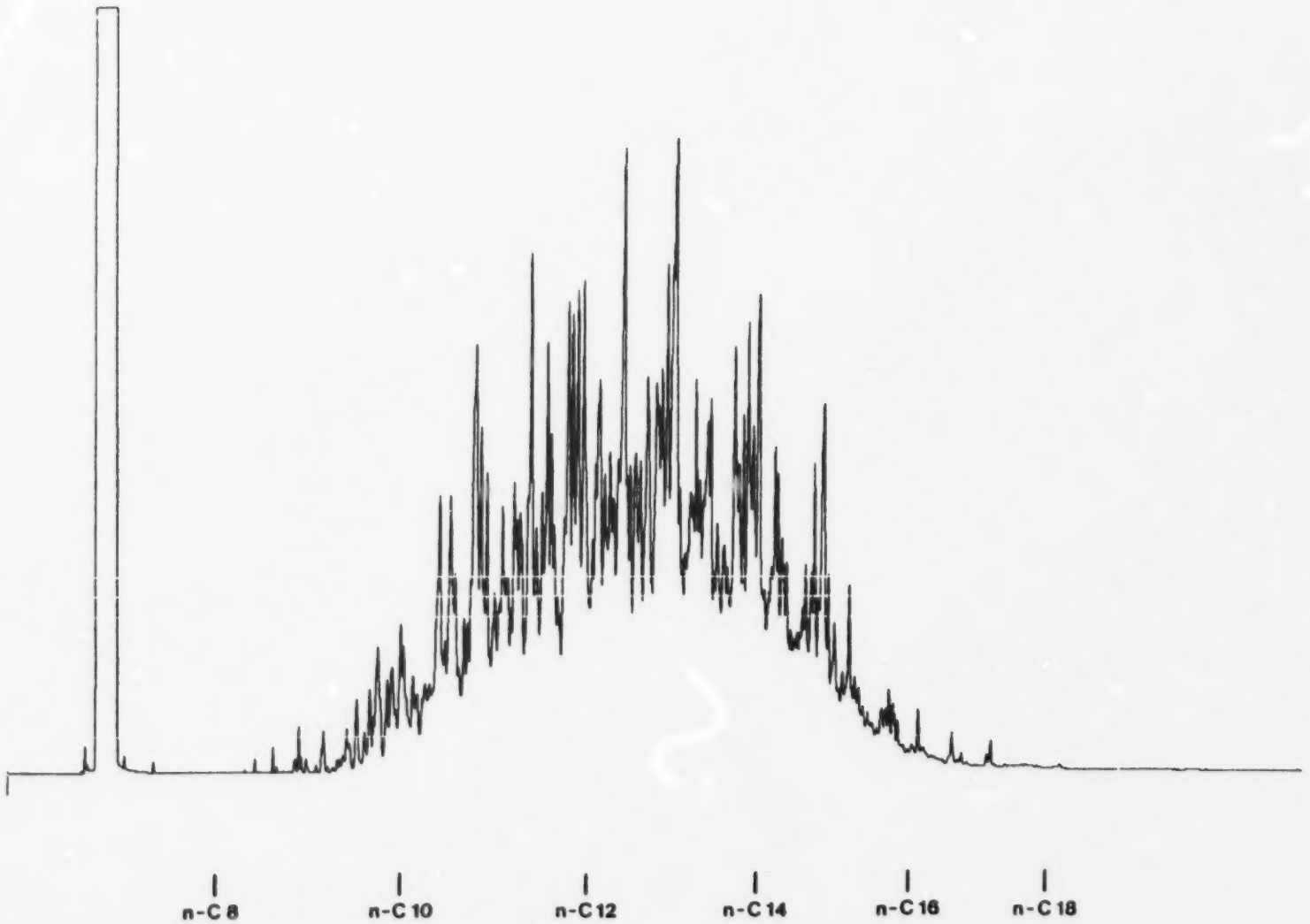


Figure 4.12 GC trace of the 15 x 10 cm surface sample of cuttings collected on Day 49 in the wave tank.

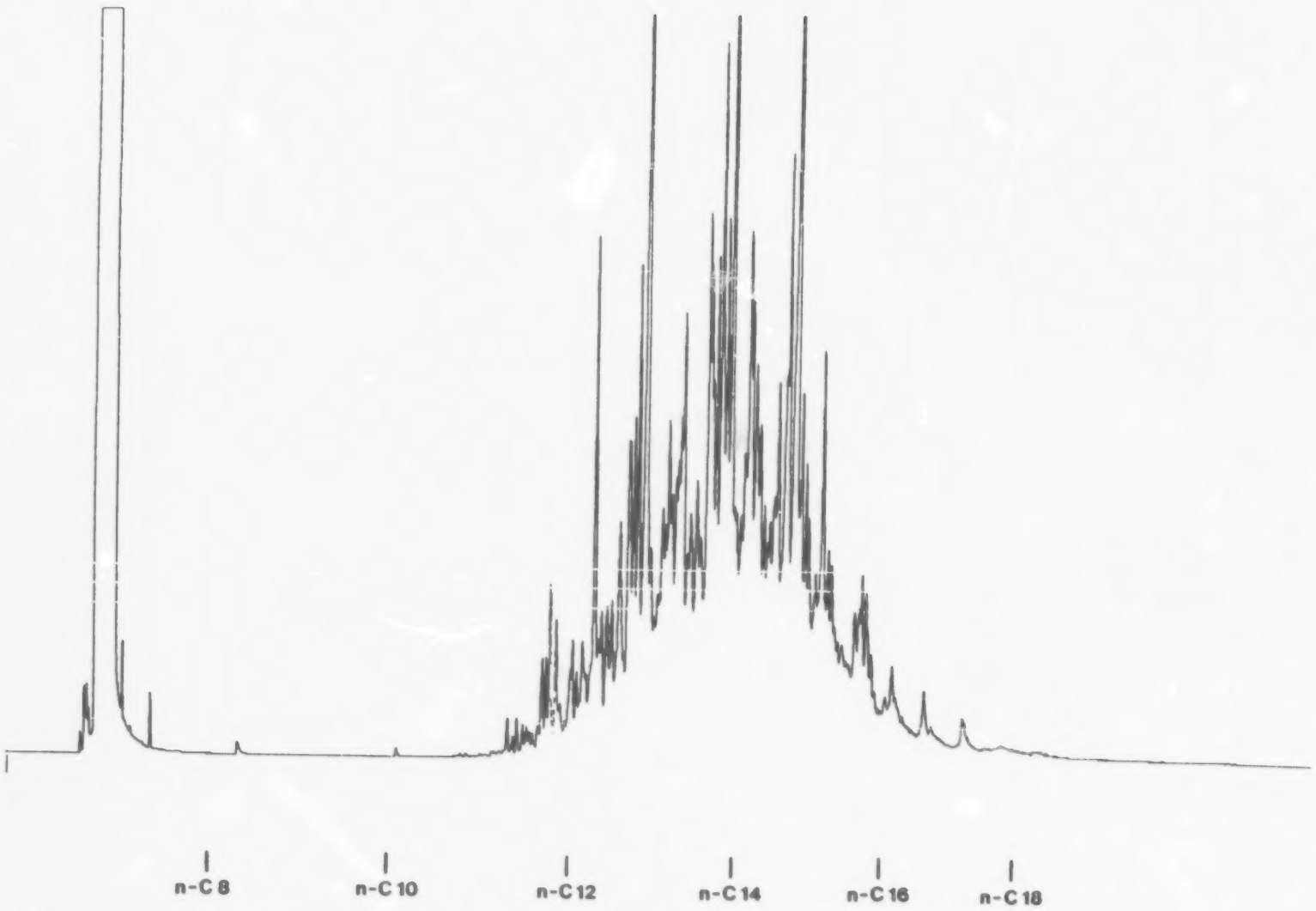


Figure 4.13 GC trace of the 15 x 10 cm subsurface sample of cuttings collected on Day 49 in the wave tank.

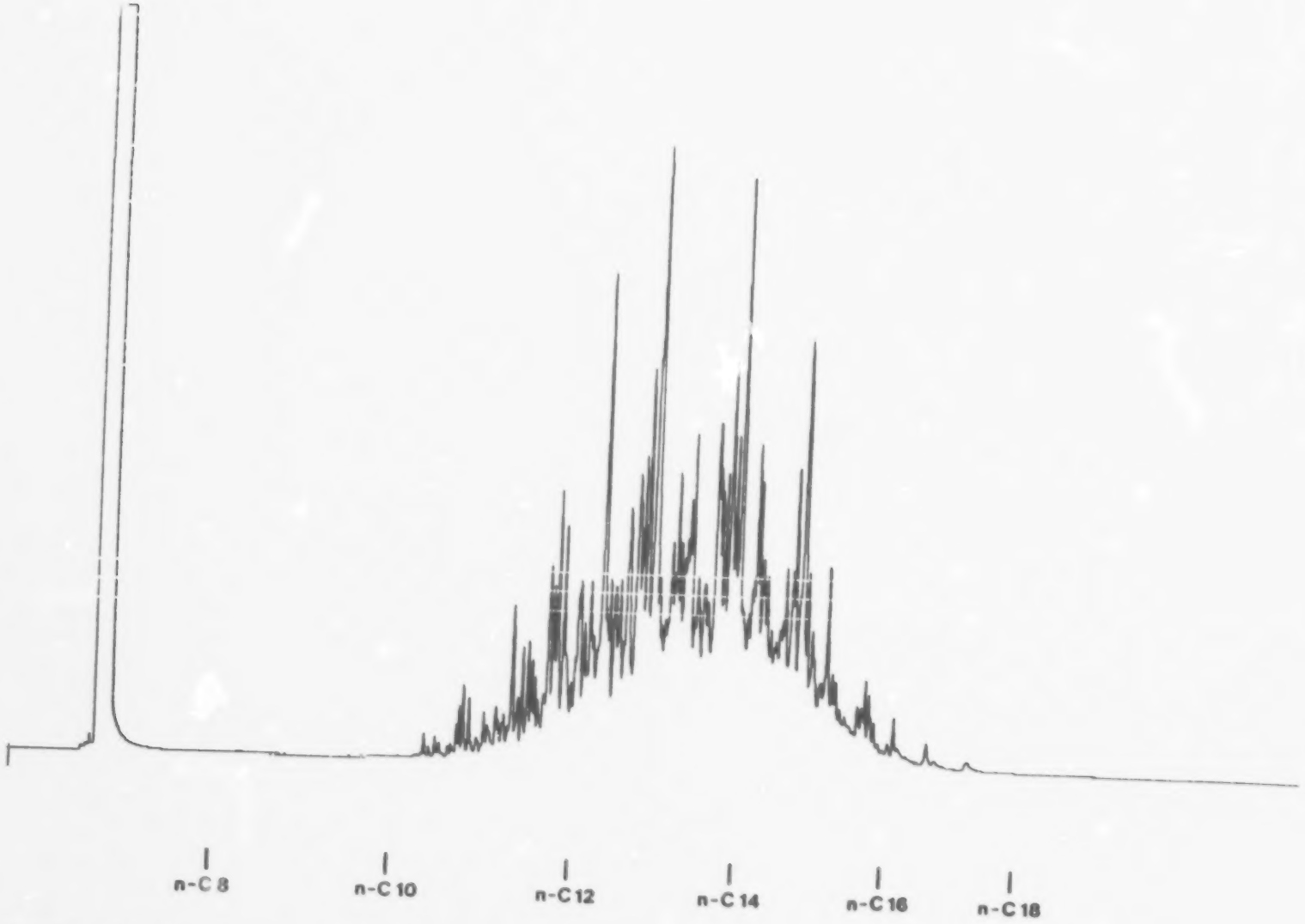


Figure 4.14 GC trace of the 110 x 10 cm surface sample of cuttings collected on Day 49 in the wave tank.

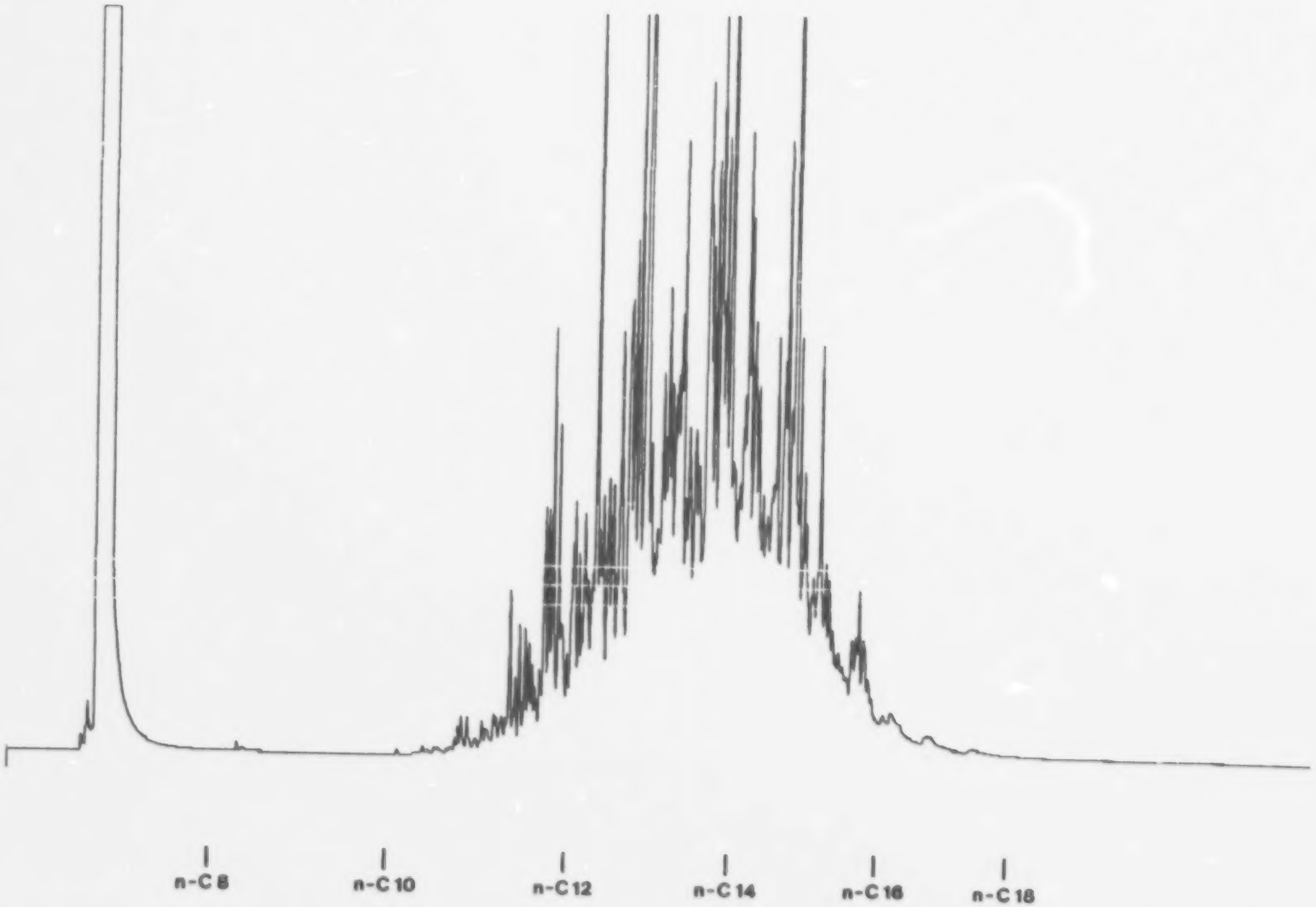


Figure 4.15 GC trace of the 110 x 10 cm subsurface sample of cuttings collected on Day 49 in the wave tank.

shown in Figures 4.13 and 4.15, the other is shown in Appendix 1). Once again, a fraction of the hydrocarbon envelope ranging from n-C9 to n-C11 has been lost and the ratio of resolved to UCM peaks has remained constant. The indication is that a discrete lower boiling fraction of the base oil is being preferentially leached out of the cuttings and that this fractionation begins in the subsurface layers of the cuttings pile. Presumably the two surface samples which showed this leaching (Days 36 and 49 in Figures 4.11 and 4.14 respectively), were from areas of the tank where the process had reached the cuttings surface. Since this process was not observed in the static tank, the indication also is that the process was accelerated by wave action. The fact that all three of the Day 49 subsurface cuttings samples showed this loss and that an ambient temperature concentration method was used makes it unlikely that the losses occurred during sample work up or handling. In addition, because the Day 49 subsurface hydrocarbon concentrations were significantly lower than the surface concentrations in the wave tank (but not the static tank; see Table 4.4 and 4.5), the conclusion can be made that this fractionation was accompanied by a general loss of oil from the subsurface cuttings layers. While it is likely that the lower boiling hydrocarbon fraction will also have a higher water solubility than the fractions that remain in the cuttings, to our knowledge this loss from the subsurface layers first has not been previously observed.

It is interesting to note that for most of the samples analyzed (with the exception of the Day 36 and 49 surface samples and the three Day 49 subsurface samples already mentioned), there were no pronounced changes in the GC traces between the wave and the static tanks. The waves thus appear to have had no effect on the hydrocarbon composition except for the perferential (mostly subsurface) leaching of a portion of the hydrocarbon envelope.

GC traces of representative wave tank samples from Days 5, 8, 19, 26 and 48 and of the other two Day 49 samples are given in Appendix 1. The GC traces all collaborate the above discussion.

4.3.2 Water Samples

The inlet seawater used for the experiments showed no indication of hydrocarbon contamination by either IR (Table 4.6) or GC (Figure 4.16).

In both the static and wave tanks, the GC traces obtained depended to a large extent on the oil concentration in the water sample. When the oil concentrations were high and there was a lot of free oil in the water sample, then the GC trace was essentially the same as the trace of the base oil (see Figure 4.4). This observation is borne out by the Day 0 water sample from the static tank (Figure 4.17; oil concentration 15,000 mg/L) and the Day 8 sample from the wave tank (Figure 4.18; oil concentration 130 mg/L).

However as the oil concentration dropped and a larger fraction of the oil was dissolved or emulsified in the water, the GC trace showed more "weathering" with a reduction in the resolved fraction and a shift in the mean hydrocarbon size to a higher molecular weight. This trend is shown by the Day 1 sample from the static tank (Figure 4.19; oil concentration 92 mg/L), the Day 48 sample from the static tank (Figure 4.20; oil concentration 16 mg/L), the Day 2 sample from the wave tank (Figure 4.21; oil concentration 4.7 mg/L) and by the Day 2 sample from the static tank (Figure 4.22; oil concentration 2.6 mg/L).

The changes in the oil composition of the water samples thus appear to be dominated by droplets of unweathered oil masking other changes. GC traces for all other water samples that had high enough oil concentrations to run on the GC are given in Appendix 2.

Figure 4.16 GC trace of the seawater inlet sample collected on Day 8.

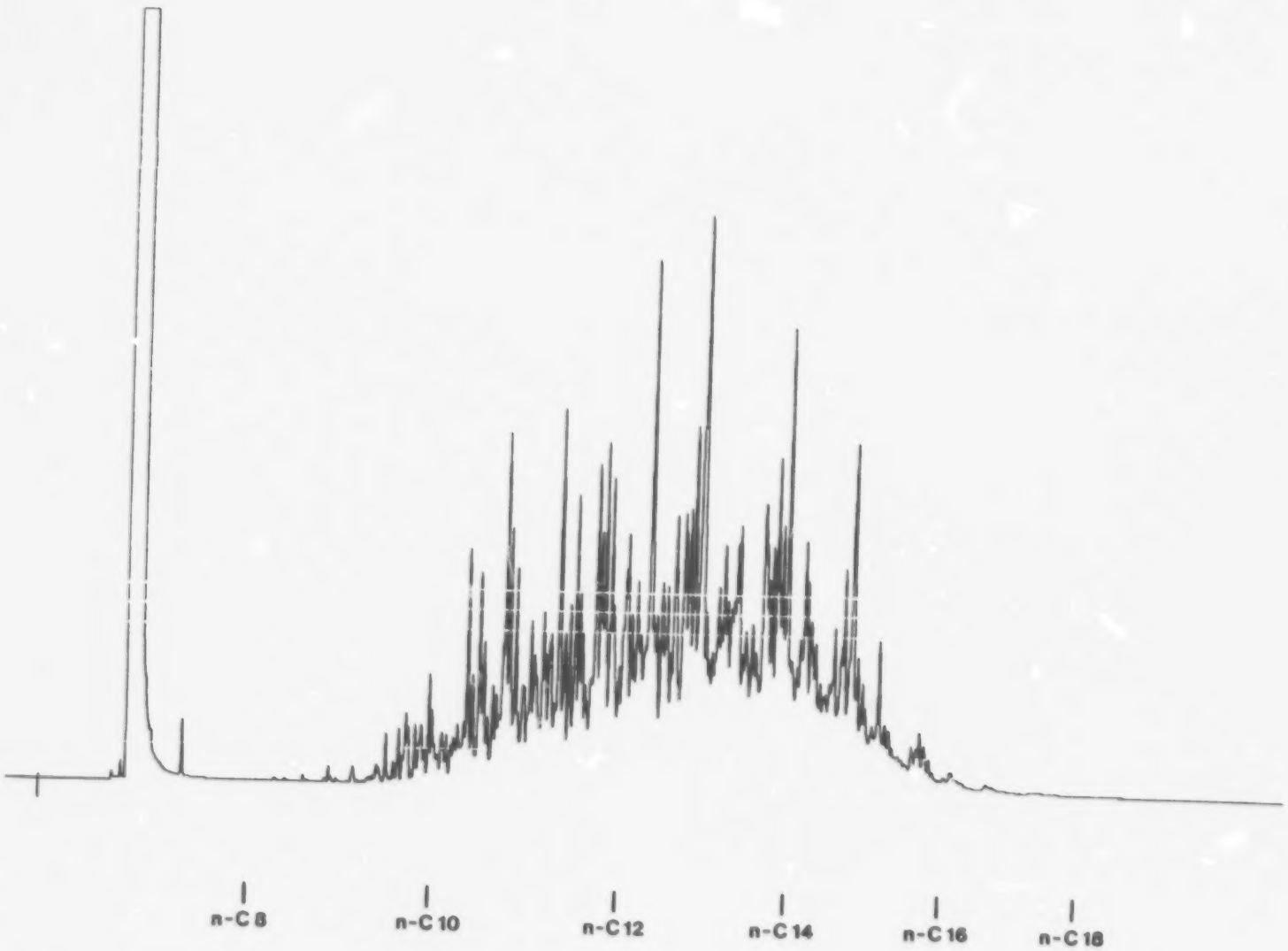


Figure 4.17 GC trace of the surface water sample collected on Day 0 from the static tank.

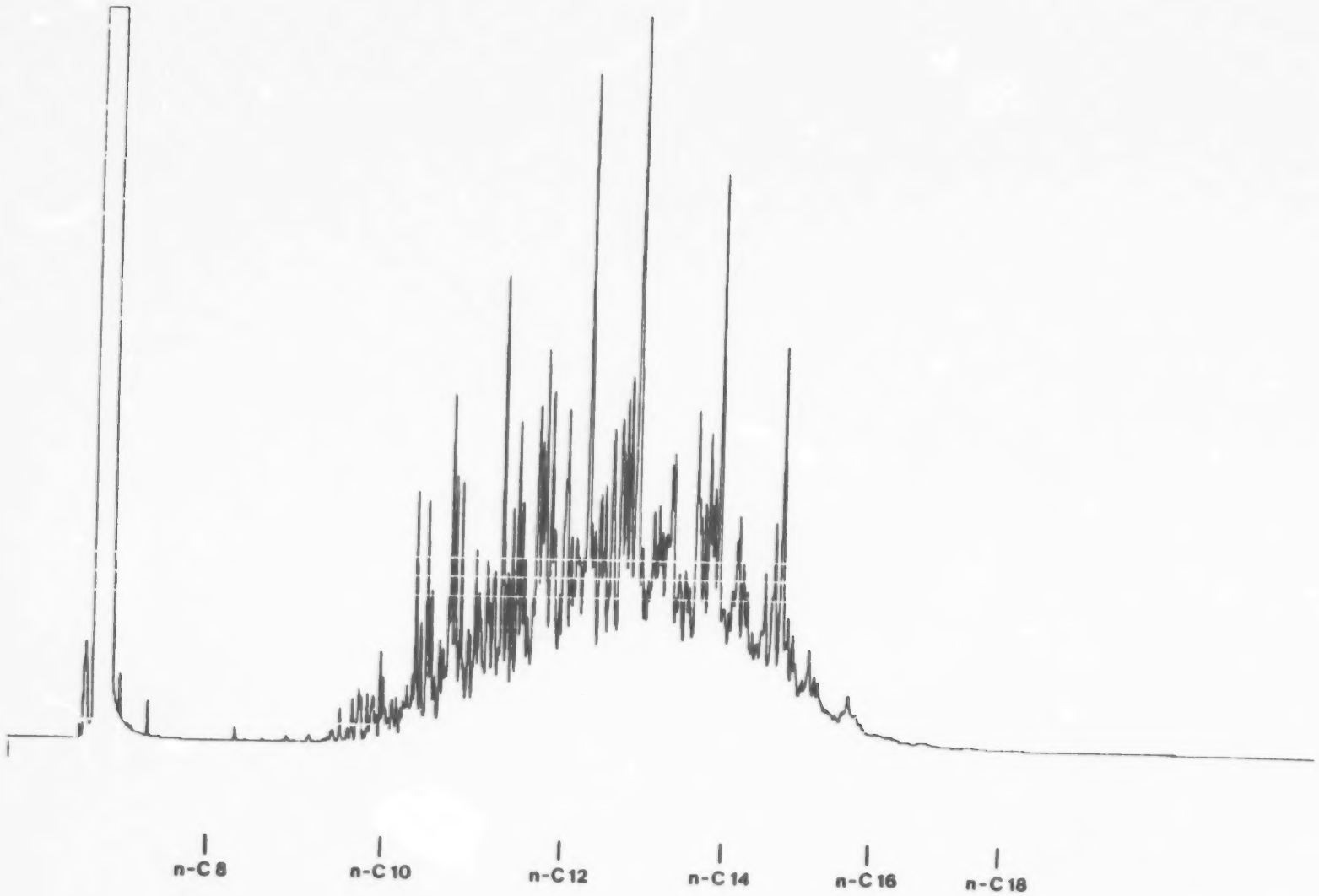


Figure 4.18 GC trace of the surface water sample collected on Day 8 from the wave tank.

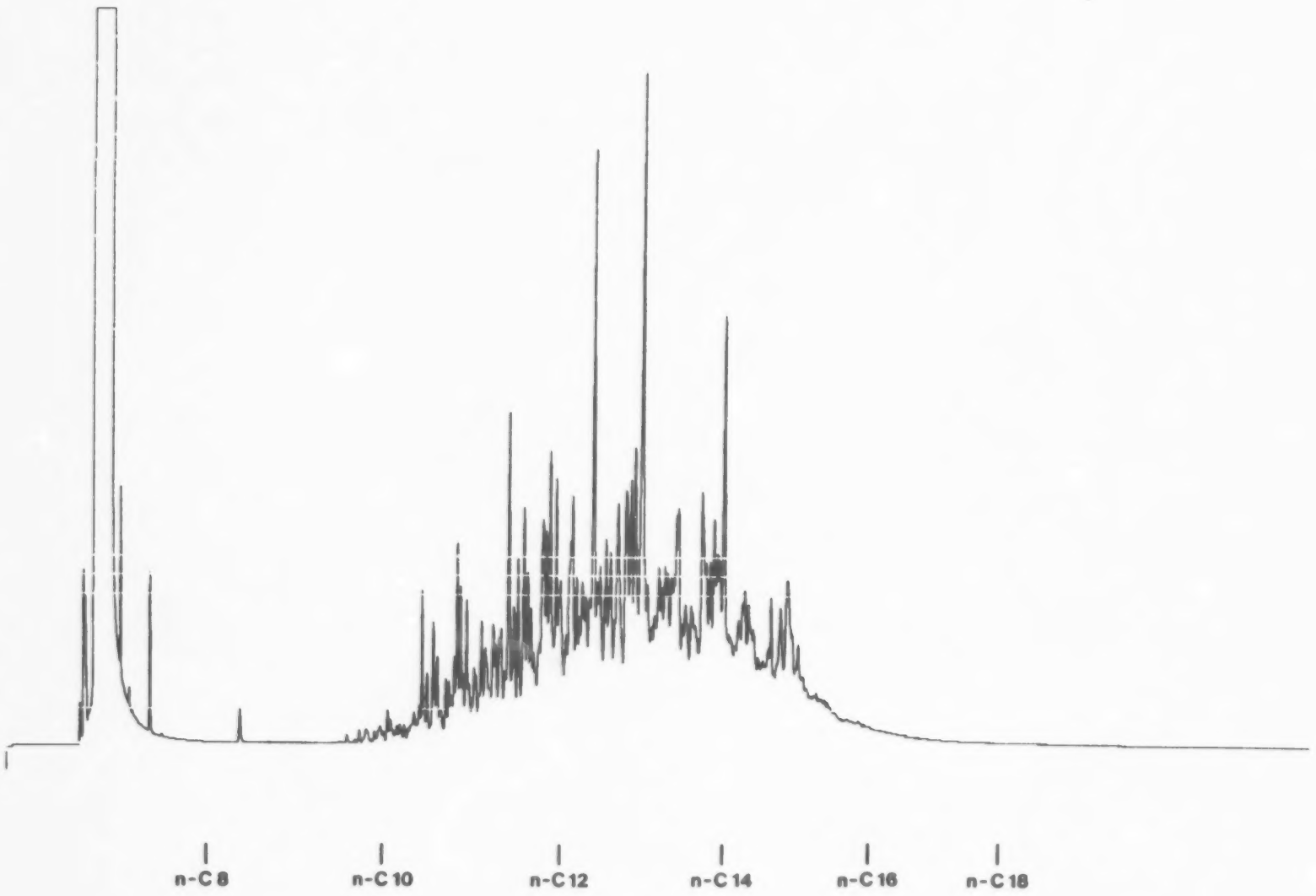


Figure 4.19 GC trace of the surface water sample collected on Day 1 from the static tank.

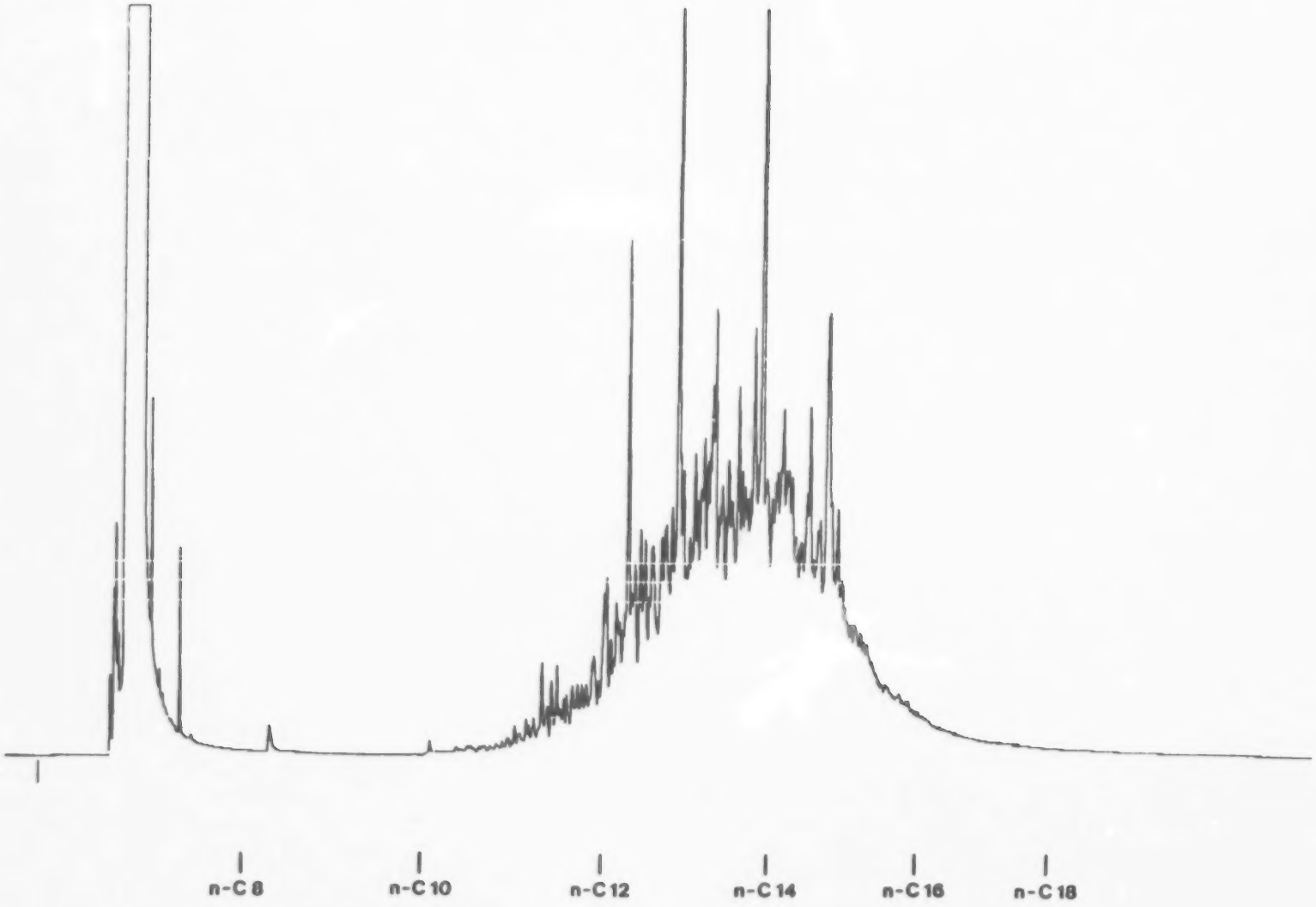


Figure 4.20 GC trace of the surface water sample collected on Day 48 from the static tank.

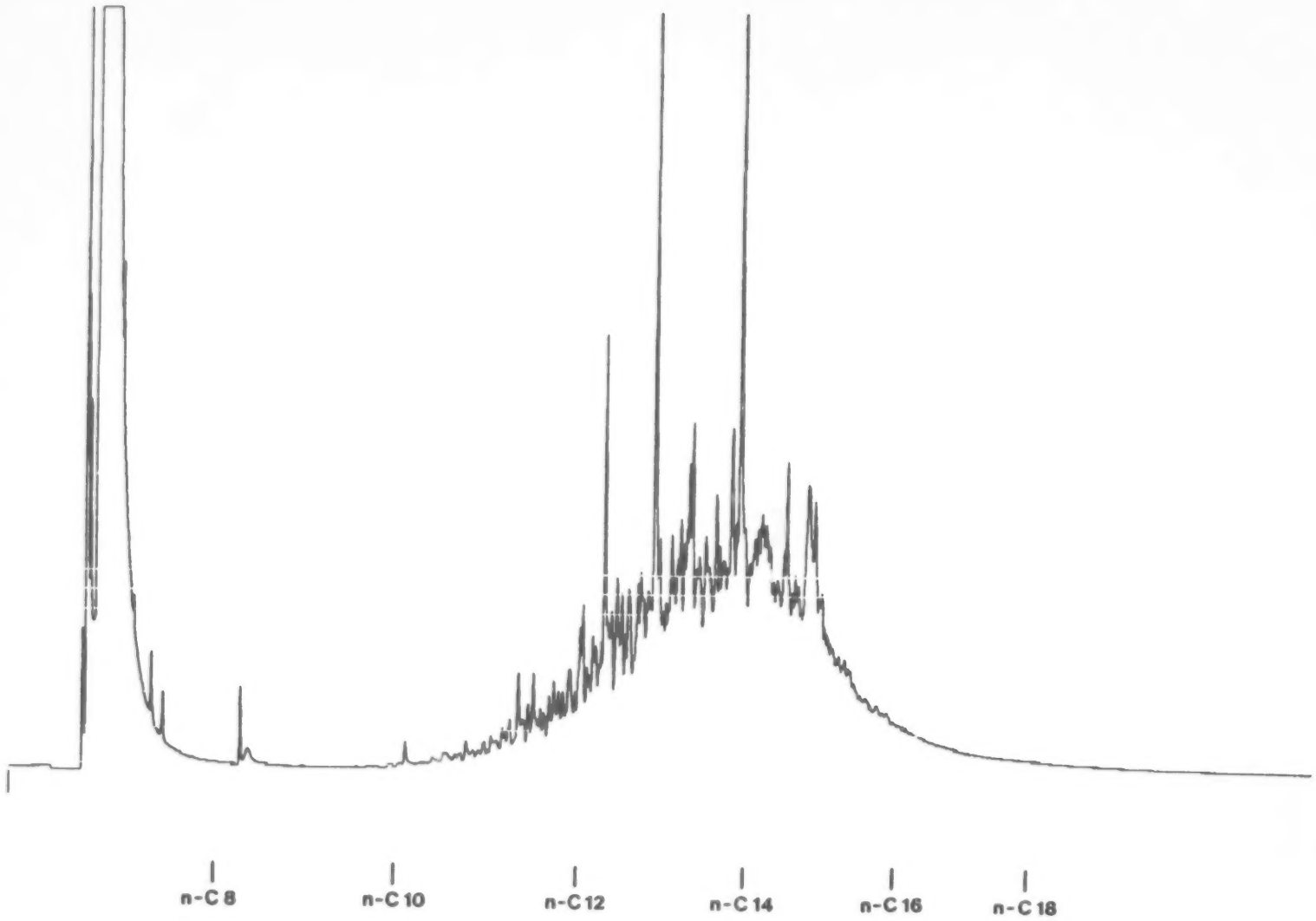


Figure 4.21 GC trace of the surface water sample collected on Day 2 from the wave tank.

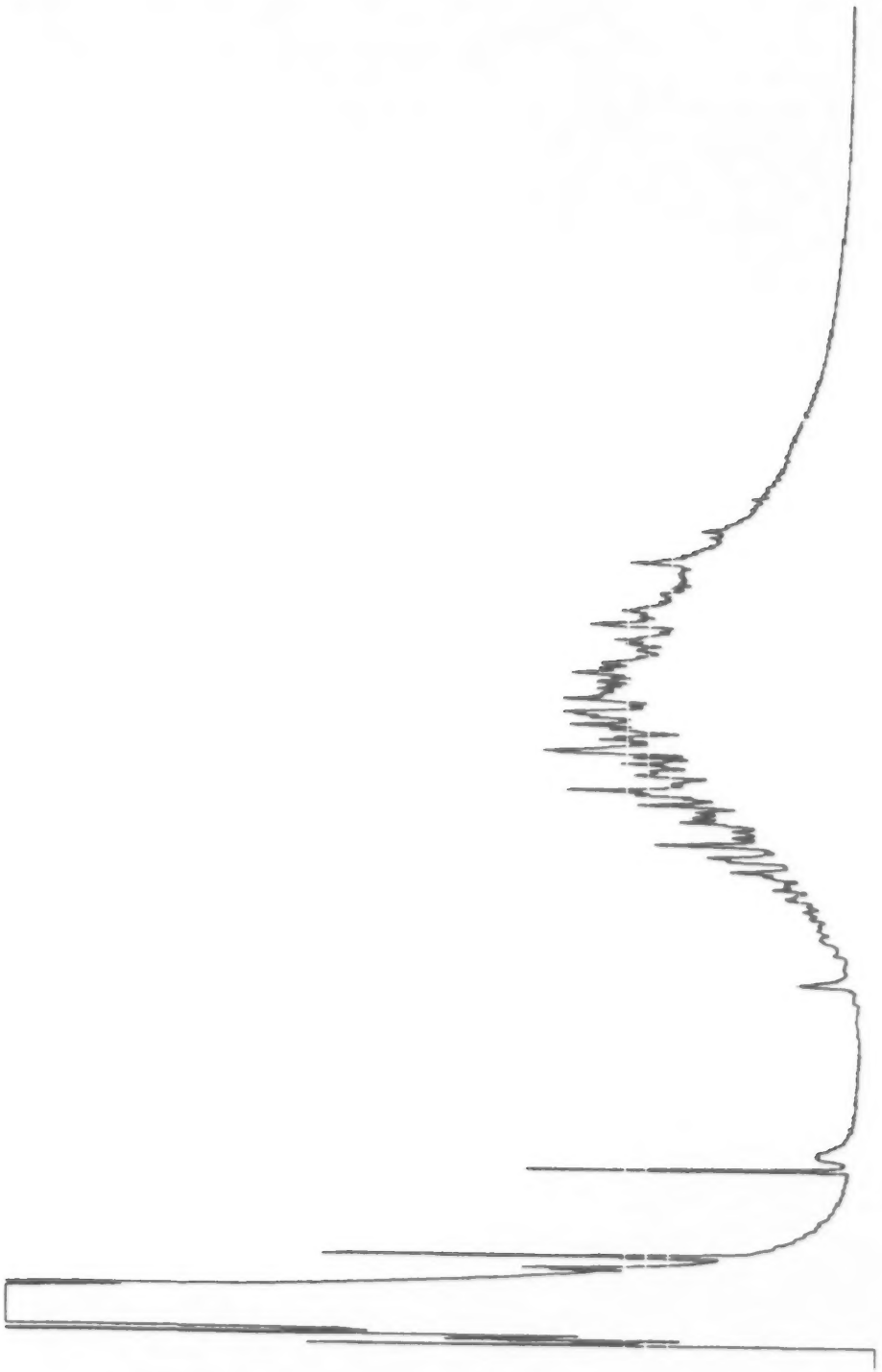


Figure 4.22 GC trace of the surface water sample collected on Day 2 from the static tank.

5.0 DETAILED EXPERIMENTAL AND ANALYTICAL METHODS

5.1 EXPERIMENTAL SET-UP AND METHODS

5.1.1 Detailed Description of Facilities

The experimental laboratory (see Figures 3.1 and 3.2) was constructed in a portable trailer (5.0 x 2.4 x 2.4 m) on the foreshore of Patricia Bay, across the road from the Dobrocky Seatech Ltd. facilities. Three tanks were constructed; the cooling bath, which housed the two experimental tanks (2.4 x 1.1 x 0.8 m), the wave tank (2.2 x 0.4 x 0.8 m) and the static tank (2.0 x 0.4 x 0.8 m).

The tanks were constructed of 3/4 in. plywood sealed with polyester resin and epoxy paint. Corners were sealed with polyester and asbestos fibre which acted as a chaulking. The large water bath was positioned in the trailer on ten 4" x 4" timbers running perpendicular to the tank. These timbers helped to distribute the weight of the tank over a greater floor area. The static tank and wave tank were positioned inside the large tank, and held in place by wooden frames on both ends. A water-tight bulkhead drain was installed near the bottom of the cooling tank. The water level in the cooling tank was regulated using a flexible pipe connected to the bulkhead; this pipe was set to the desired vertical height before passing through the floor of the trailer to discharge onto the foreshore. Styrofoam insulation (5 cm) was put on the outside of the outer cooling tank to aid in temperature regulation.

Seawater was supplied to the trailer by an intake line (76 m long and 3 cm diameter) made of utility grade polyethylene. The line was fitted with a screened foot valve and set at 2 m below lower low water. Weights were positioned along the length of the pipe to hold it on the bottom. A 3/4 HP jet pump inside the trailer delivered water to the 130 L constant head reservoir set on an aluminum stand. The level of water in the reservoir

was controlled to within ± 0.5 cm using an electronic fluid level control which controlled operation of the pump. The constant head reservoir allowed accurate adjustment of the water flow to the tanks using simple plastic ball valves. From the reservoir a supply line of 0.6 cm I.D. polyethylene ran into a 7.6 m section of I.D. copper tubing placed inside the water bath. The copper tubing had been baked for two hours at 450°C with a flush of high purity nitrogen to clean the line of any hydrocarbons. The copper line was used to precool the seawater being delivered to the test tanks. From the copper tubing a polyethylene line branched to two independently controlled lines running to the two test tanks. Two ball valves controlled the water flow to an inlet manifold in each test tank. The manifold was made of branched polyethylene tubing to maximize uniformity of flow through the tanks.

Water flow into each tank was kept at about 1 L/min which provided one water change every 10 - 12 hours. Water height in the tanks was maintained at 0.5 m (0.3 m below the top) by outlets at the other end of the tanks. Bulkhead fittings were used to connect the outlets to the outside of the cooling bath tank. The outlets were fitted with valves for water sampling. They were connected to a filter cannister containing polyurethane foam absorbant material to remove any suspended or dissolved oil from the water before discharge to the foreshore.

Double racks of acrylic egg crates were fastened to the bottom about 30 cm from the end of each tank. In the static tank, the egg crates were orientated vertically, while in the wave tank they were orientated on an angle to help dampen the waves. In both tanks, a 15 cm high piece of plastic was attached to the bottom of each rack of egg crates to contain the oily cuttings. The wave generator was positioned in the slightly longer wave tank (2.2 vs 2.0 m for the static tank) so that the oiled cuttings bed size was exactly the same size in both tanks. Plastic vials (an assortment of sizes from 20 to 50 mL volume) were placed behind the egg crate in the wave tank (on the end opposite the wave generator) to dampen the waves.

The wave generator consisted of two 1/8" aluminum plates held 2.5 cm apart with reinforcing aluminum struts and anchored to the bottom of the wave tank with wooden pillow block bearings. The wave generator extended 14 cm above the top of the tank and was 34 cm wide, leaving only 1.5 cm of space between the tank wall and the aluminum plates on either side. The top of the generator was connected to two short push rods that were loosely bolted together and then connected by bearings to an aluminum cam wheel. This cam wheel controlled the length of the stroke of the plate. The cam was powered by a 3/4 Hp motor equipped with a 20/1 reduction drive. This drive was connected to the cam shaft by a chain and sprockets. With the wave generator positioned 34 cm from the end of the tank, and the slanted egg crates at both ends, this left a 140 x 37 cm bed for introduction of drill cuttings. The effective length of the tank bottom in the static tank was made the same length by adjusting the position of the vertical egg crates.

5.1.2 Modifications to Experimental Facilities During the Experiment

On Day 6 of the experiment, bats of 10 cm fiberglass insulation sealed in heavy polyethylene were placed on top of the experimental tanks. The bearings were also replaced in the wave generator assembly to allow for small amounts of sideways movement.

Intermittent problems were experienced with the tanks overfilling, especially with the wave tank. The problem was finally traced to blockage of the valves in the outlet lines by particulate material. On Day 27 these two valves were removed and the problem disappeared.

5.1.3 Mixing of the Oiled Cuttings

Five 20 L plastic pails of oily drilling mud cuttings, containing a total of about 80 L, were collected by INAC personnel at the Adgo G-24 wellsite and shipped to the Dobrocky Seatech Ltd. facilities in Sidney, B.C. The cuttings were received in good order on or about January 21, 1986.

A new cement mixer was used for mixing the oiled cuttings; oily residues remaining from manufacturing or shipping were removed by wiping down the

inside with acetone soaked paper towels. Initially about 30-40 L of oiled cuttings were added to the mixer (this was its practical capacity) and well mixed. A portion of this material was then removed and replaced by new cuttings. This procedure was repeated numerous times over a three hour period until all of the oiled cuttings had passed through the mixer many times. At this point the oiled cuttings were transferred back into the five 20 L pails and transported across the street to the experiment site. The cuttings material was then added haphazardly to each tank, ensuring that the same volume of oiled cuttings was added to both tanks. The mixing and addition was carried out on January 23, 1986 (Day -6).

It was observed that even with these elaborate mixing procedures, the coarse cuttings would rapidly settle and oily water containing visible oil droplets would pool on the top of each bucket. In addition it was difficult to ensure that the same amount of "free" oil was present in each bucket. One composite sample of the well mixed oily cuttings was collected from both the static and wave tanks immediately after the cuttings were added to each tank.

5.1.4 Experiment Start

On January 29, 1986 (Day 0), the outer tank was filled with crushed ice and addition of seawater to each tank was commenced through the copper cooling coil. This proved to be too slow and so the majority of the filling was done via a line (2.5 cm id) directly from the seawater resevoir. At 16:30 a sample was taken of the first water to flow out of each tank. Large amounts of free oil were observed floating on the water surface (a dark brown color) in the static tank, but only a little oil was observed on the water surface in the wave tank. This difference was attributed to the amount of "free" oil present in each tank at the point when the water was added. The wave generator was started at this time and the water formed a brown emulsion. However, the waves proved to be a little too large (the sides of the tanks showed excessive buckling) and the wave generator was left off overnight.

On Day 1 (January 30), the wave stroke was shortened, extra reinforcing was added to the sides of the wave tank and extra plastic vials were added to

the wave damper behind the acrylic egg crate. The wave generator was then restarted with much better results. Two hours after the wave generator had been restarted, the water was oily but not emulsified, and at this time one could barely see the bottom. This poor visibility appeared to be due to fine particulate material in suspension and not due to oil emulsion. After this time the wave generator was only off for short periods of time either for sampling or minor repairs.

On Day 1, the static tank was now clear with spots of oil floating on the water surface. At this time, dark brown oily spots had also formed on the cuttings surface that were to persist to the end of the experiment. Significant events for the experiment are given in Table 5.1.

5.1.5 Sampling Protocol

Water samples were taken by removing a replacable plug in each outlet line from both the wave and static tanks and collecting a 2-4 L sample (see Table 3.1). Since water flowed out of the tanks through an overflow port, this meant that the sample collected would be taken from the surface water of each tank. Water samples were also collected from the seawater intake so that the hydrocarbon background level could be established. Oven baked (400 °C) bottles were used for the collection of all samples.

In the first few days of the experiment an attempt was made to collect cuttings samples by a number of coring procedures. Insertion of a full length core tube (i.e. longer than the water plus sediment depth) into the tank allowed the collection of a cuttings sample, but on retrieval, the water in the tube rushed out the bottom of the core and an intact sample could not be collected. More success was obtained with a short (15 cm) core tube; the tube was pushed into the tank sediment, capped with a core cap by reaching down into the water, withdrawn to the sediment surface and a metal plate slid under the bottom of the tube. Poor visibility in the wave tank made this a difficult procedure to carry out, since the cold, oily water made it hard to properly collect the sample "by feel". In addition, the unconsolidated nature of the oily cuttings and the tendency

Table 5.1 Significant Events for the Experiment

Date	Day	Comments
Jan. 21	-8	Adgo G-24 oiled cuttings received.
Jan. 23	-6	Cuttings well mixed and added to static and wave tanks.
Jan. 29	0	Tanks filled with water (Initial temperature 5°C). Large amounts of oil on water surface in static tank and small amounts in wave tank. Static tank dark brown, wave tank brown emulsion. Wave generator on for <1h.
Jan. 30	1	Extra bracing added to the sides of the wave tank, extra plastic vials added to wave damper and wave stroke modified. Wave generator started at 13:45. Static tank clear and oily; wave tank oily but not emulsified (one could barely see the bottom).
Feb. 3	5	Light sheen of oil on surface of wave tank; water murky and visibility limited. Static tank clear with 1 cm clumps of oil on both the surface of the water and cuttings and dark oil sticking to the tank sides.
Feb. 15	17	Wave tank murky, static tank clear, both covered with a light oily film.
Feb. 16	18	Oily film now absent on wave tank.

Table 5.1 Significant Events for the Experiment (Continued)

Date	Day	Comments
Feb. 17	19	Wave tank still murky with a few oil spots on the surface. Static tank unchanged.
Mar. 01	31	Static tank showed an oil film on surface. Wave tank less murky but bottom still not visible; small amounts of oil on surface.
Mar. 03	33	Could now just see the bottom of the wave tank.
Mar. 18	48	Two small holes found in copper inlet line; they would have been present less than 1 day.
Mar. 19	49	Film of oil on static tank, with visible oil globules. Only a very light oil sheen on wave tank with a slight haze in the water.

of the water collected in the core to run out the bottom, made it very difficult to collect an intact sample. An additional sampling device was constructed by cutting off about half of the side of a 1 L plastic bottle and fastening the remainder of the bottle (including the intact bottom) to a strip of plastic. This bottle was then lowered through the water to the surface of the cuttings and was then gently moved across the surface of the cuttings so that an intact sample was obtained of the top 1-2 cm of the sediment. With a little care, the sample was only collected from an area the size of the diameter of the bottle. It was then quite easy to lift the bottle back up to the surface, pour off the water and transfer the cuttings sample to a cleaned (oven baked at 400 °C) bottle.

The latter procedure allowed the collection of an undisturbed sample of the cuttings surface from the bottom of each tank. Since this was the area of a cuttings pile that would actively leach oil into the water column, it was quite important that an undisturbed sample of this active layer be collected. A random number generator was used to select locations for sampling in each tank and an effort was made not to sample any location twice. The area within 5 cm of the side was also avoided to eliminate any influence of the tank walls on the samples.

In order to prevent the discharge of oily water into Patricia Bay, the overflow water from both tanks was passed through a canister containing a plastic oil adsorbant before being allowed to flow back into the bay. This oil absorbant was changed periodically (see Table 3.1).

The sampling schedule is given in Table 3.1. In most cases triplicate samples of the cuttings were collected on each sampling day. In using the detailed sample collection matrix (which provides sampling positions in each tank for each cuttings sample) measurements were made lengthwise from the end of the cuttings bed opposite from the wave generator and widthwise from the edge of the tank closest to the center of the cooling bath (see diagram in Section 3.3).

5.1.6 Measurements of Oiled Cuttings Resistance

A marine cone penetrometer, the Sea Cone, was used to measure the resistance and hardening of the oiled cuttings over the course of the experiment. The Sea Cone system was developed by Dobrocky Seatech Ltd. for Russel Parrot of the Atlantic Geosciences Center and was designed to be used with the Pisces IV submersible (Imber, 1985). For this work only the 10 cm^2 cone tip (containing the load guages), the control box and a digital multimeter were used.

At the start of the experiment, the oiled cuttings in the experimental tanks were very unconsolidated and the 10 cm^2 cone (the largest available) sank through the cuttings bed without measureable resistance. Accordingly, the penetrometer was modified by inserting a 20.2 cm diameter plexiglass disk into the head of the cone, thereby increasing the load bearing surface area to 325 cm^2.

To take a penetrometer measurement, the clean probe was immersed in the tank and held suspended just above the cuttings bed. It was necessary to hold the penetrometer very steady at this point so that the output voltage signal could be adjusted to zero using the penetrometer control box. When the display had been adjusted to zero and was stable, the penetrometer was dropped into the mud cuttings and the maximum number displayed by the multimeter was taken as the resistance reading. After the reading was taken, the penetrometer was removed from the cuttings, adhering mud was removed and the procedure was repeated in the other tank. Measurements obtained are given in Table 4.2.

Note that the resistance being measured by this procedure is the resistance of only the top layer (1-2 cm) of the oiled cuttings bed. Because of the very shallow nature of the cuttings bed (7 cm) it was necessary to modify the penetrometer so that it would almost "float" on the cuttings; in this way, contact with the tank bottom did not interfere with the resistance measurement. As a result, any hardening or consolidation of the cuttings

in the subsurface layers of the cuttings bed would not be detected by this technique. Also, since the penetrometer was large (over 20 cm diameter) in comparison to the total surface area of the cuttings bed, multiple measurements could not be made without excessively disturbing the cuttings surface, and potentially jeopardizing the rest of the experiment. To minimize this disturbance most of the measurements were confined to the end of each tank furthest from the wave generator.

5.2 ANALYTICAL METHODS

The extraction method for seawater and oiled cuttings was adapted from Conrad et al. (1984). They described a simple rapid method for the quantitative determination of drilling fluid base oils in oiled cuttings and seawater samples. The method used infra-red spectroscopy (IR) for the quantitation of the amount of oil in the sample.

Freon (1, 1, 2-trichlorotrifluoroethane; BDH Omnisolv or Chemonics pesticide grade) was substituted for carbon tetrachloride as the extracting agent because of its higher volatility and lower toxicity. It was expected that Freon would be able to provide quantitative extraction (Levy, 1986, pers. comm.); carbon tetrachloride is usually required when higher molecular weight hydrocarbons ("high ends") are to be extracted, but the base oil used does not contain measurable amounts of these fractions.

All sampling containers, glassware and aluminum foil were baked at 400-450°C for a mininum 2 h before use. Volumetric glassware and plastic scoopulas were soaked in RBS detergent, and rinsed with hot water, methanol (two times) and Freon (three times) before use. Filter papers and Teflon film were soaked in Freon and rinsed with Freon before use.

An IEC International Centrifuge model UV was used to centrifuge cuttings extracts. Infra-red analyses of Day 0 to Day 8 water samples were performed on a Perkin-Elmer 337 IR spectrophotometer leased from a Victoria firm while all other water samples and all cuttings samples were analyzed on a Perkin-Elmer 1320 IR spectrometer at the University of Victoria. Beckman 30-300 1 cm quartz cells were used on both instruments. GC analyses were performed using a Varian 3700 GC with capillary injector, a

Vista 401 data system and flame ionization detection. Splitless injection was used and the column was a 0.25 mm ID x 30 m DB5 fused silica column obtained from J and W Scientific.

5.2.1 Seawater Samples

Seawater samples were extracted three times with Freon (100 mL and 2 x 50 mL) in the 2 L or 4 L sampling bottles. The bottles were shaken for exactly 1 min, allowed to settle, and the Freon drawn out of the bottom of the bottle into a 500 mL Erlenmeyer flask using Teflon tubing and a propipette bulb. The combined Freon extracts were dried over oven baked sodium sulfate, concentrated by evaporation at or near room temperature, and made up to volume in 50 or 100 mL volumetric flasks.

5.2.2 Cuttings samples

Cuttings samples were thawed, mixed thoroughly using a plastic scoopula and subsampled. First, a 2 g subsample (weighed to 0.001 g) was weighed into a pre-weighed crucible (with lid), dried at 105 °C for 12 h and then ashed at 450°C for over 4 h. The final sample weight was used to calculate the ash weight; the ash weight was used to express the oil content of the cuttings on a dry weight basis.

Second, a 10 g subsample (weighed accurately) of the cuttings was measured into a tared 150 mL beaker and covered with aluminum foil until extraction. Freon (50 mL) was added to the beaker, the sample was well mixed with an aluminum scoopula and the slurry was decanted into four 20 mL centrifuge tubes. The extracts were centrifuged for 20 min at 3000 rpm and the supernatant was decanted and vaccum filtered through two Whatman number 1 filter papers in a Buchner funnel. The extraction and centrifugation procedure was repeated twice more (2 x 50 mL Freon) and the filter papers were washed with one further portion (50 mL) of Freon. The combined extracts were allowed to concentrate at room temperature, were dried over sodium sulfate and transferred to 50 or 100 mL volumetric flasks.

5.2.3 Infra-red analysis

A sample of Conoco ODC base oil that was supplied to Dobrocky Seatech Ltd. by Technifluids Ltd., was used to prepare standard samples with concentrations of 25, 50, 75, 100, 200, 250 and 300 mg/L. These standard samples were used to quantify the infra-red (IR) response in terms of the base oil concentration. Final results were expressed in terms of Conoco ODC mineral oil extracted from the cuttings sample in mg/g ash weight or from the water samples in mg/L.

Volumetric flasks and stoppers were weighed before and after an aliquot was removed for analysis, so that a correction could be made for loss of Freon if the sample had to be reanalyzed. Most cuttings extracts were diluted a further 50 or 100 fold before analysis. Dilution was not required for most of the water extracts.

A scan range of 3200-2700 cm^{-1} was used. The baseline and slit width of the IR spectrometer were adjusted using Freon in both the sample and reference 1 cm quartz cells. Samples were then analyzed with the cells being rinsed three times between analyses. If the C-H stretch at 2950 cm^{-1} was less than 20% transmittance, the sample was diluted and reanalyzed. Sets of Conoco ODC oil standards were analyzed at the beginning, middle and end of each lot of samples analyzed. Calibration data are given in Table 5.2.

Water samples from Day 0 to Day 8 were analyzed on the Perkin-Elmer 337 IR. All other water samples and all cuttings samples were analyzed on the Perkin-Elmer 1320 IR.

5.2.4 Gas Chromatography

The Varian 3700 GC instrument conditions used are as follows:

Gases:

Carrier:	Helium High Purity 2 mL/min
Make-up:	Nitrogen Prepurified 30 mL/min
Detector:	Air 300 mL/min
	Hydrogen 25 mL/min

Table 5.2 Infra-red Calibration Data

For Day 0 to Day 8 Water Samples (Perkin-Elmer 337 IR).

$$\text{IR Absorbance} = 0.88122 \times 10^{-3} \times \text{Conoco oil concentration} + 0.021197$$

$$r = 0.9926$$

For Day 12 to Day 49 water samples and all cuttings samples (Perkin-Elmer 1320 IR).

$$\text{IR Transmittance} = 0.25191 \times 10^{-2} \times \text{Conoco oil concentration} + 0.015968$$

$$r = 0.9993$$

Temperature:

Injection port:	250 °C
Detector:	350 °C
Column oven:	40 °C, hold for 1 min, 40° - 290° @ 8 °C/min

A Hamilton 7101N one uL syringe equipped with a Chaney adaptor was used for all injections. A custom made syringe guide was attached to the septum retainer nut of the GC and used to ensure the reproducibility of syringe needle placement for all analyses.

Before each injection the syringe was washed at least three times with dichloromethane, rinsed at least three times with the sample to be injected, the syringe pumped three times to remove air bubbles and the plunger drawn up to 1 uL. The septum purge was turned off, the sample injected over 10 sec and the temperature program was started. The syringe needle was removed from the septum guide after 10 sec and rinsed at least ten times with dichloromethane. The septum purge was turned on again after 1 min.

The column was normally baked out at 240 °C overnight with all FID gases flowing.

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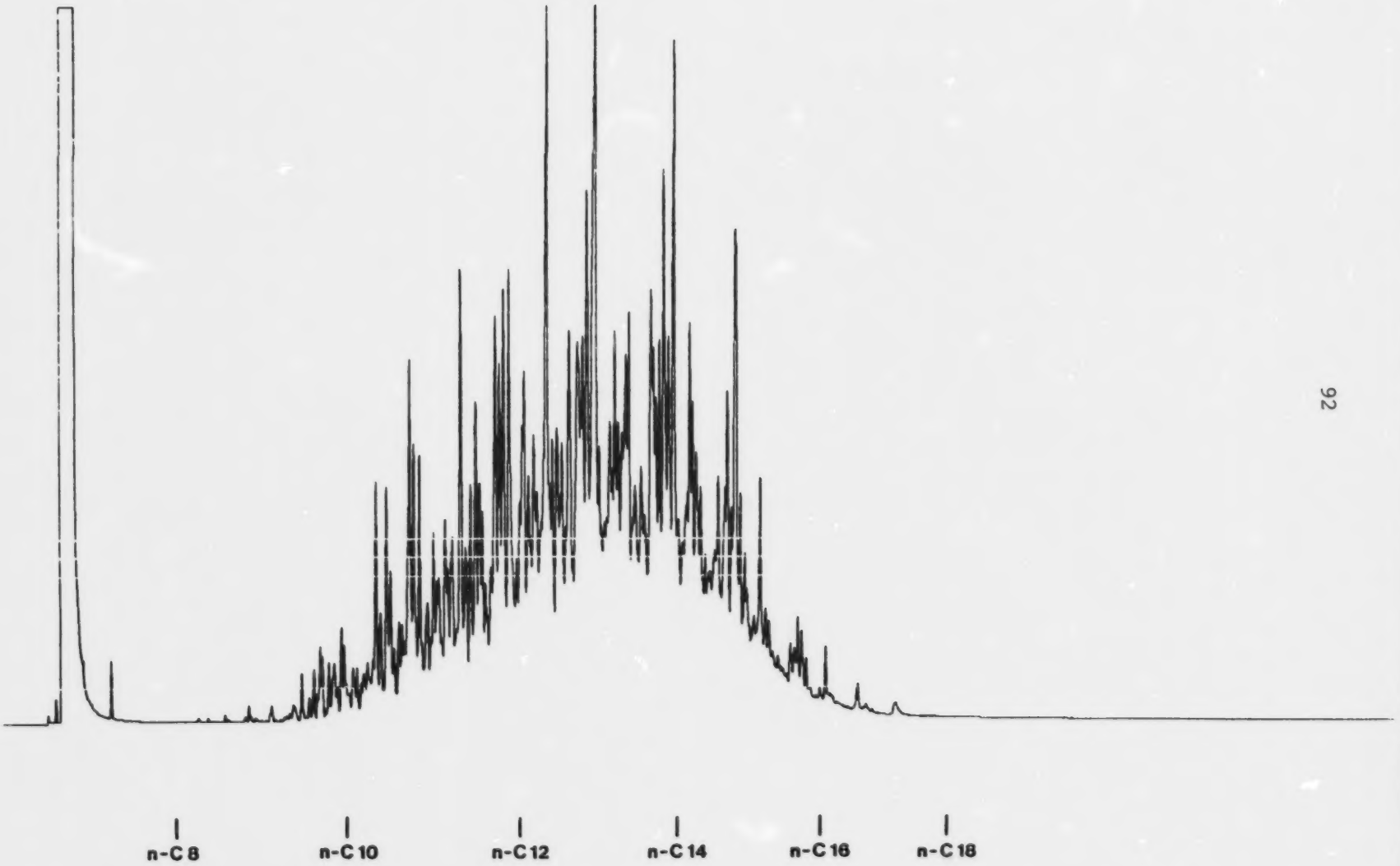
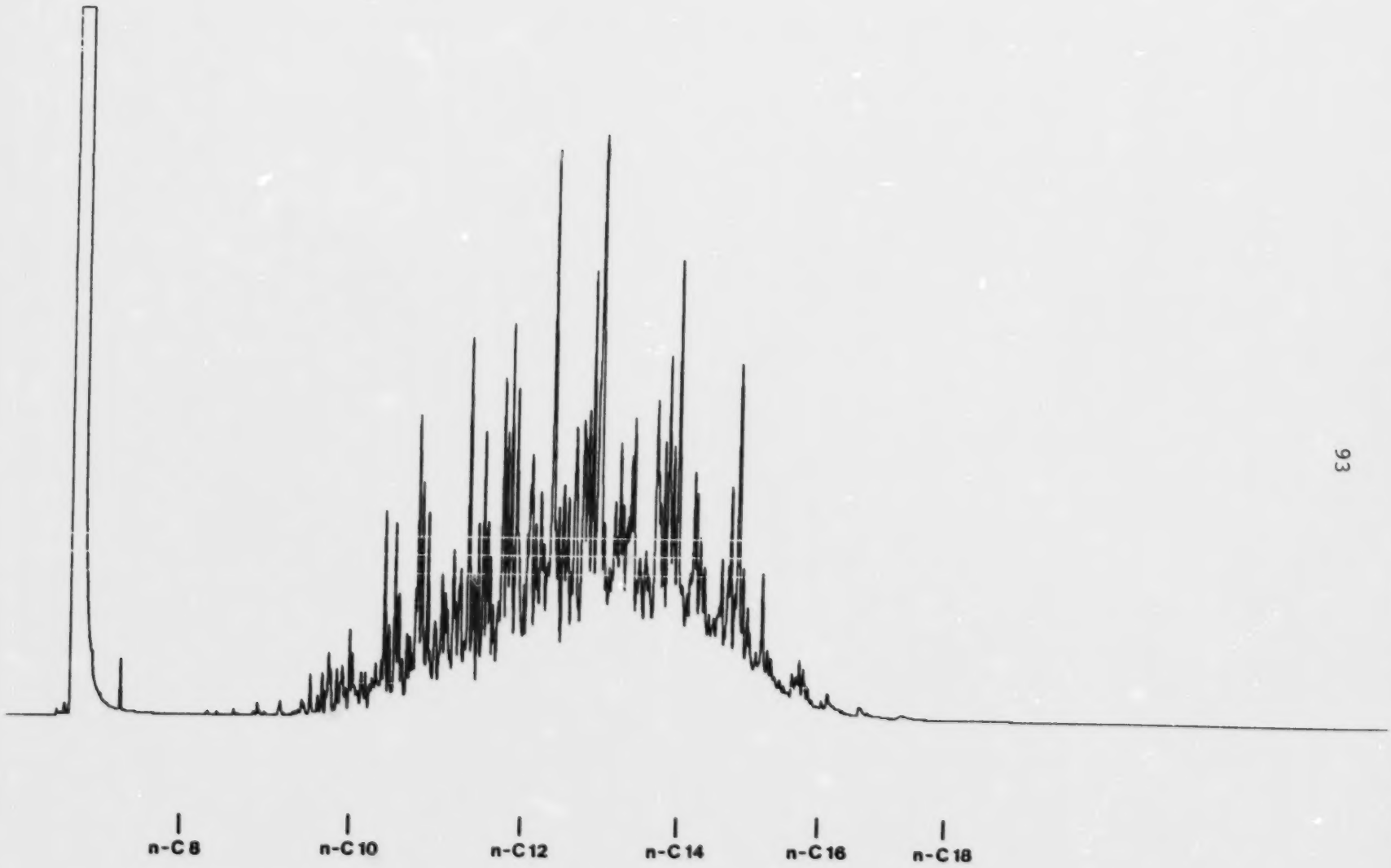
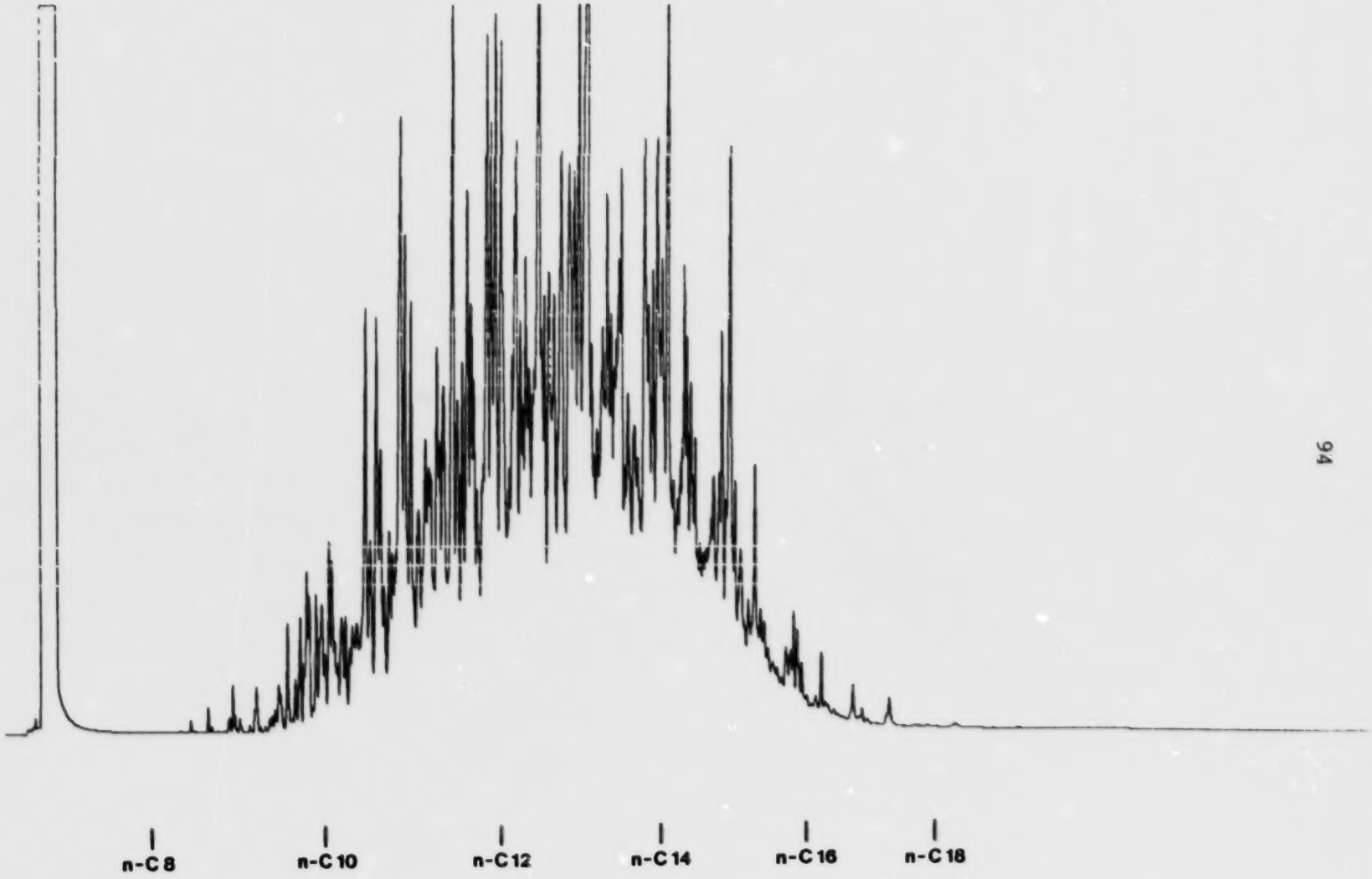
GC Traces of Cuttings Samples



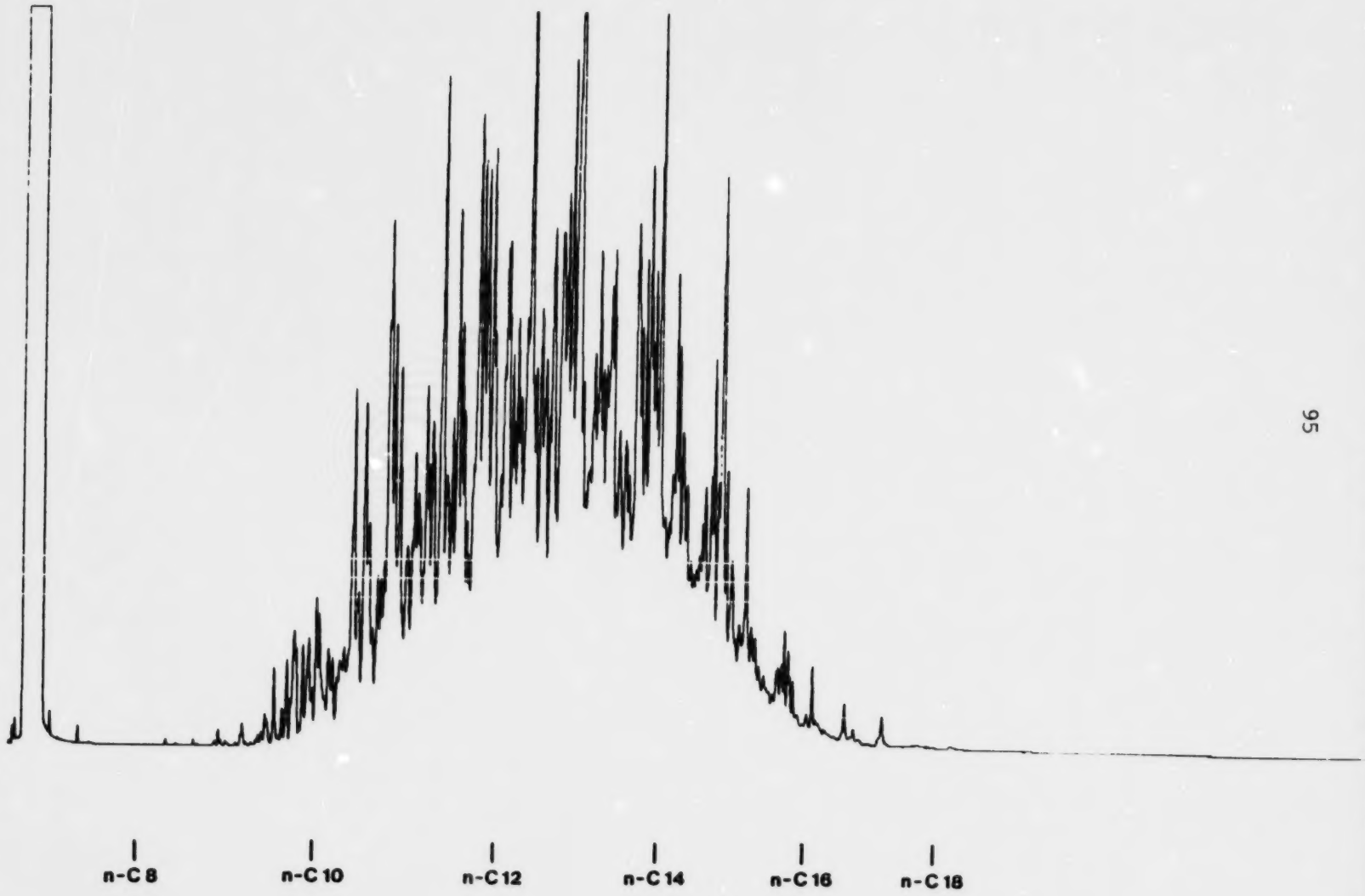
GC trace of the 80 x 15 cm surface sample collected on Day 8 from the static tank.



GC trace of the 110 x 10 cm surface sample collected on Day 5 from the static tank.



GC trace of the 60 x 30 cm surface sample collected on Day 19 from the static tank.



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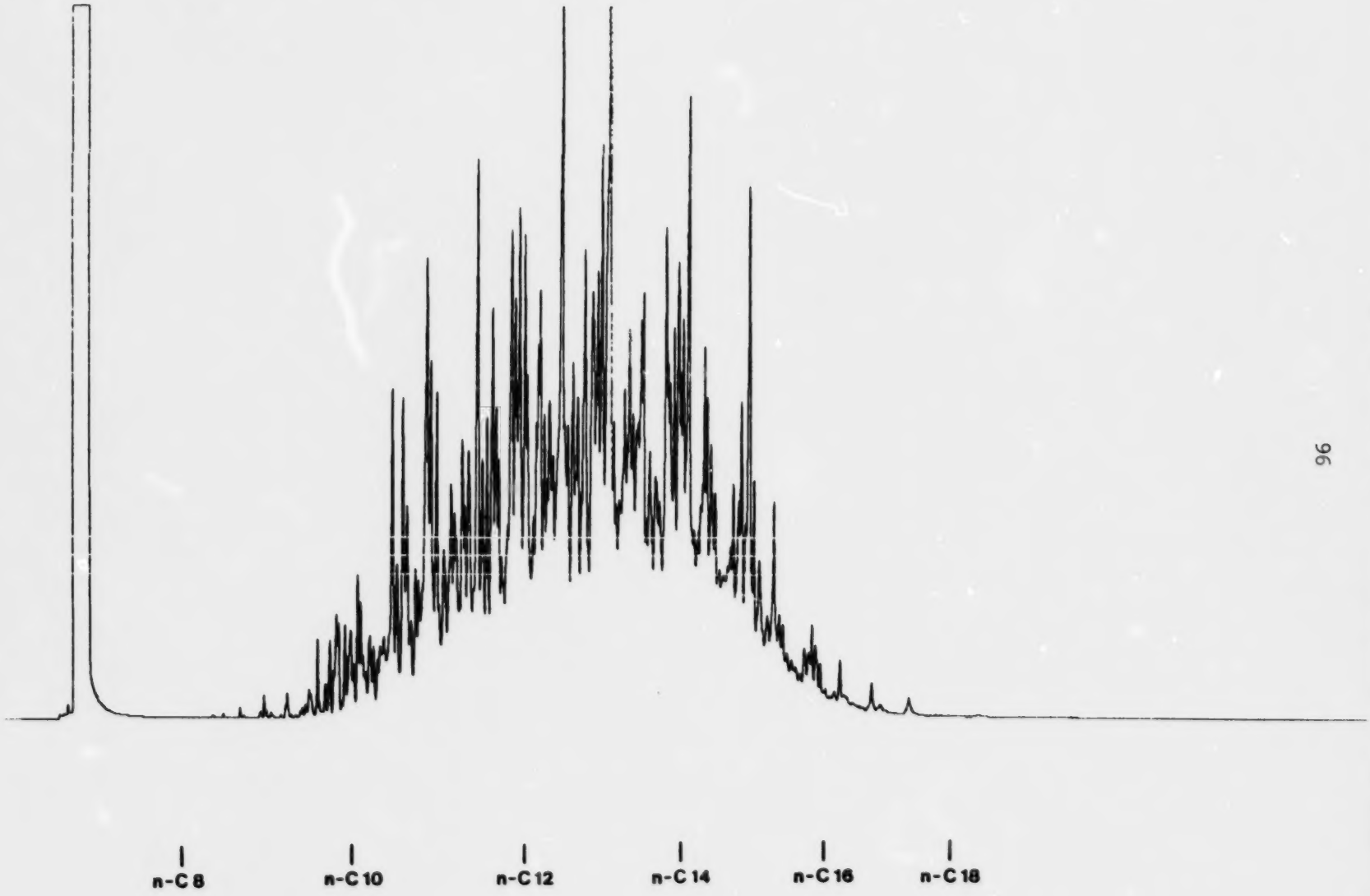
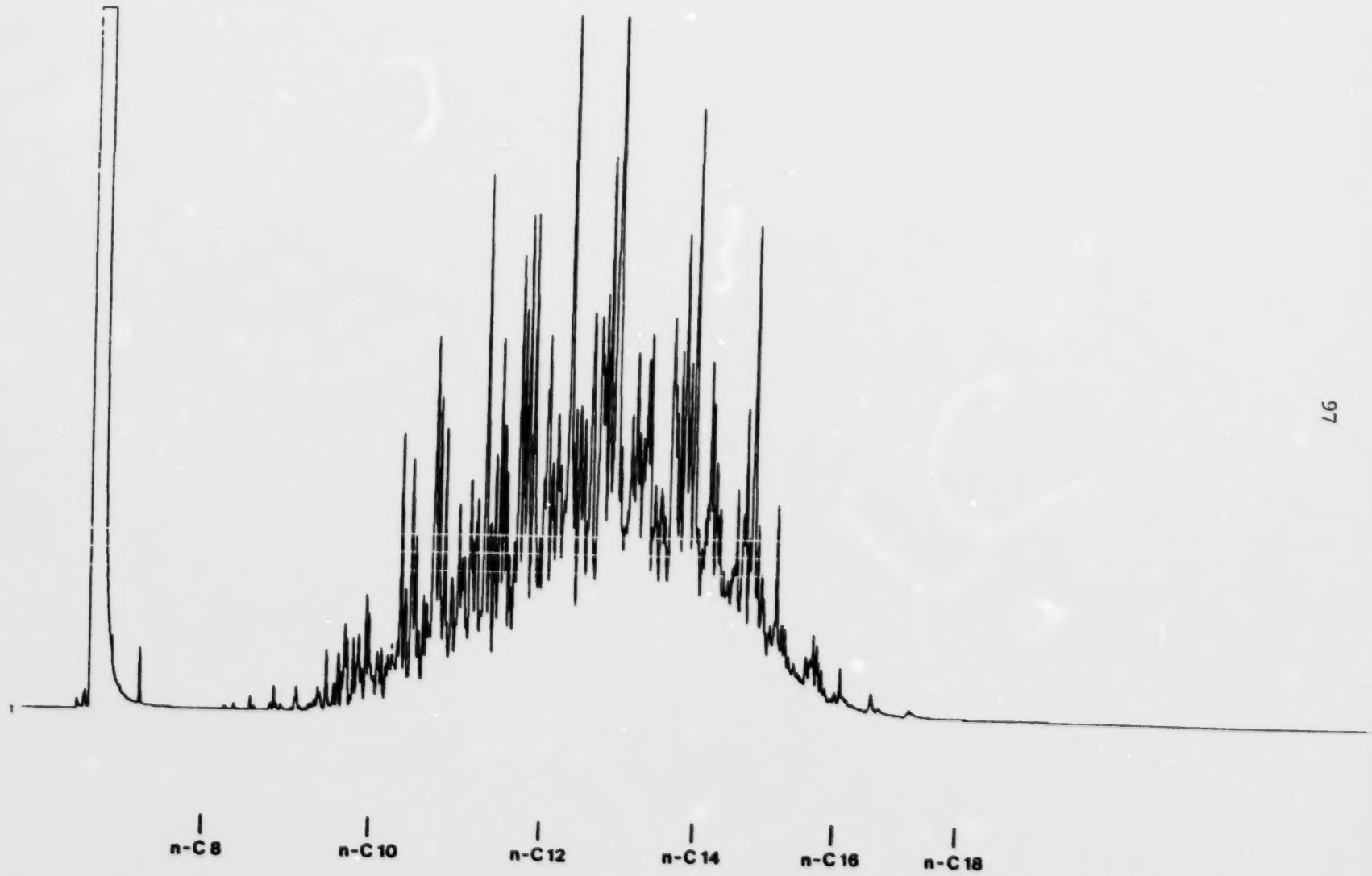
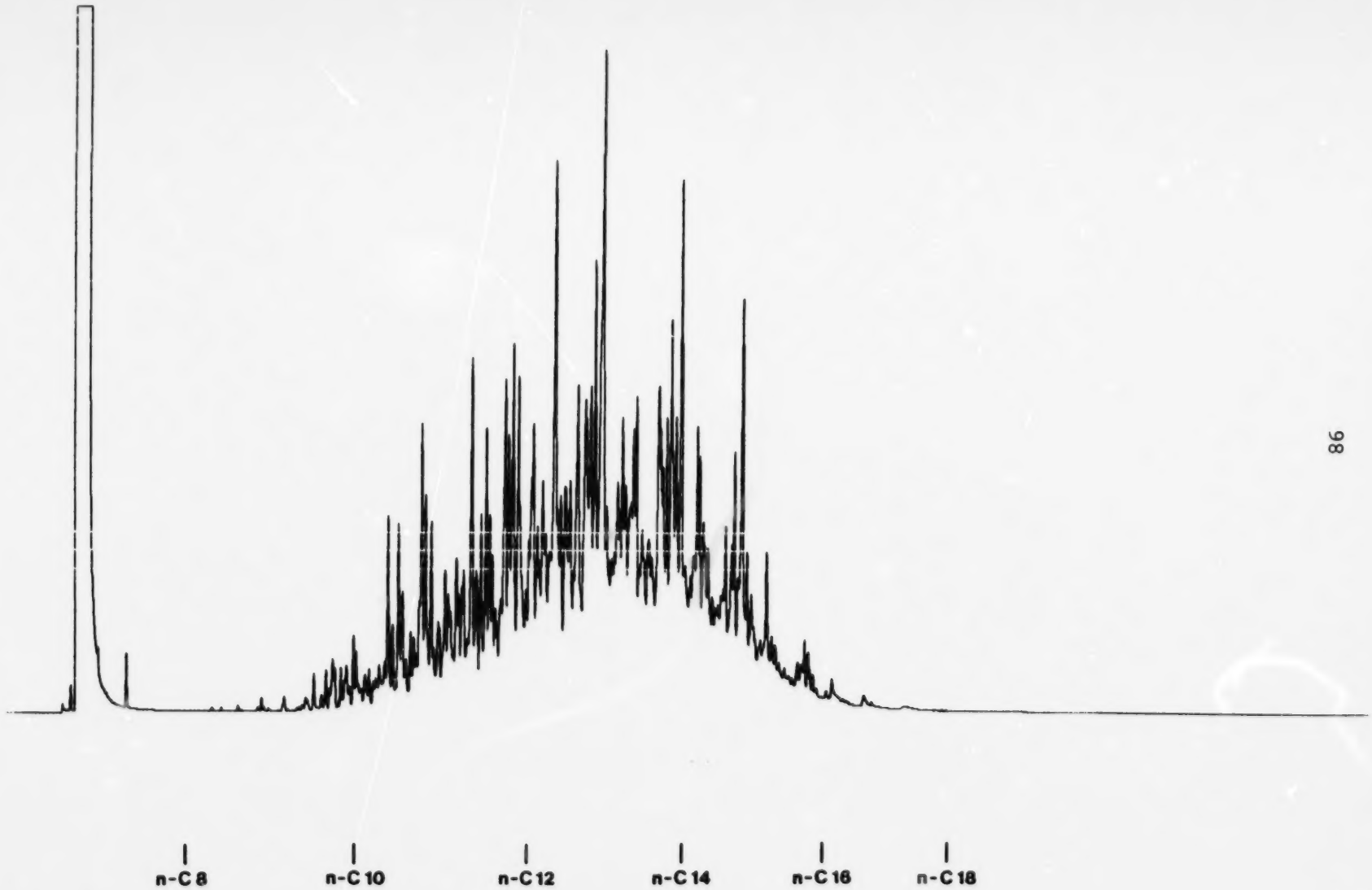


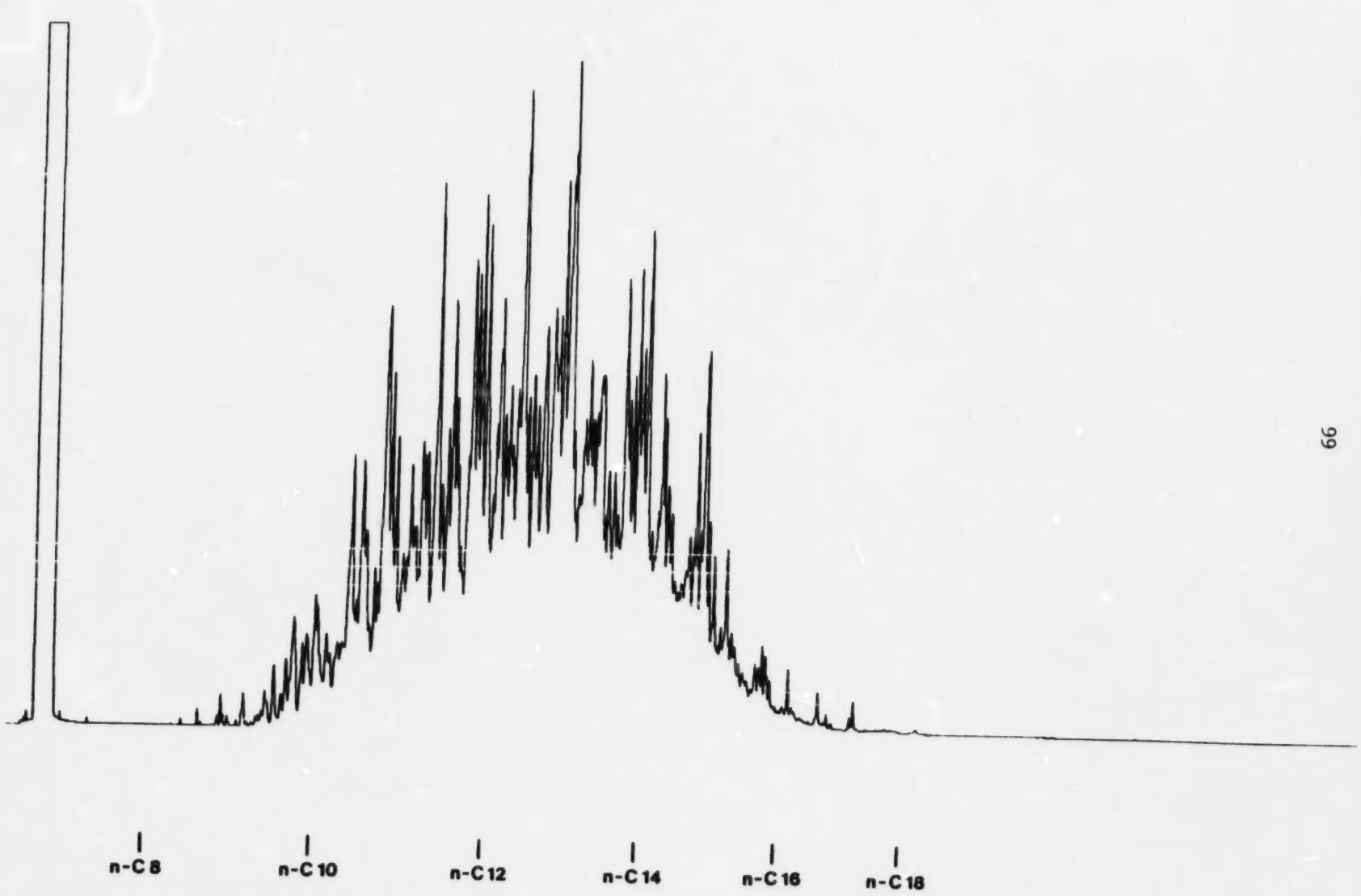
GC trace of the 60 x 10 cm surface sample collected on Day 48 from the static tank.



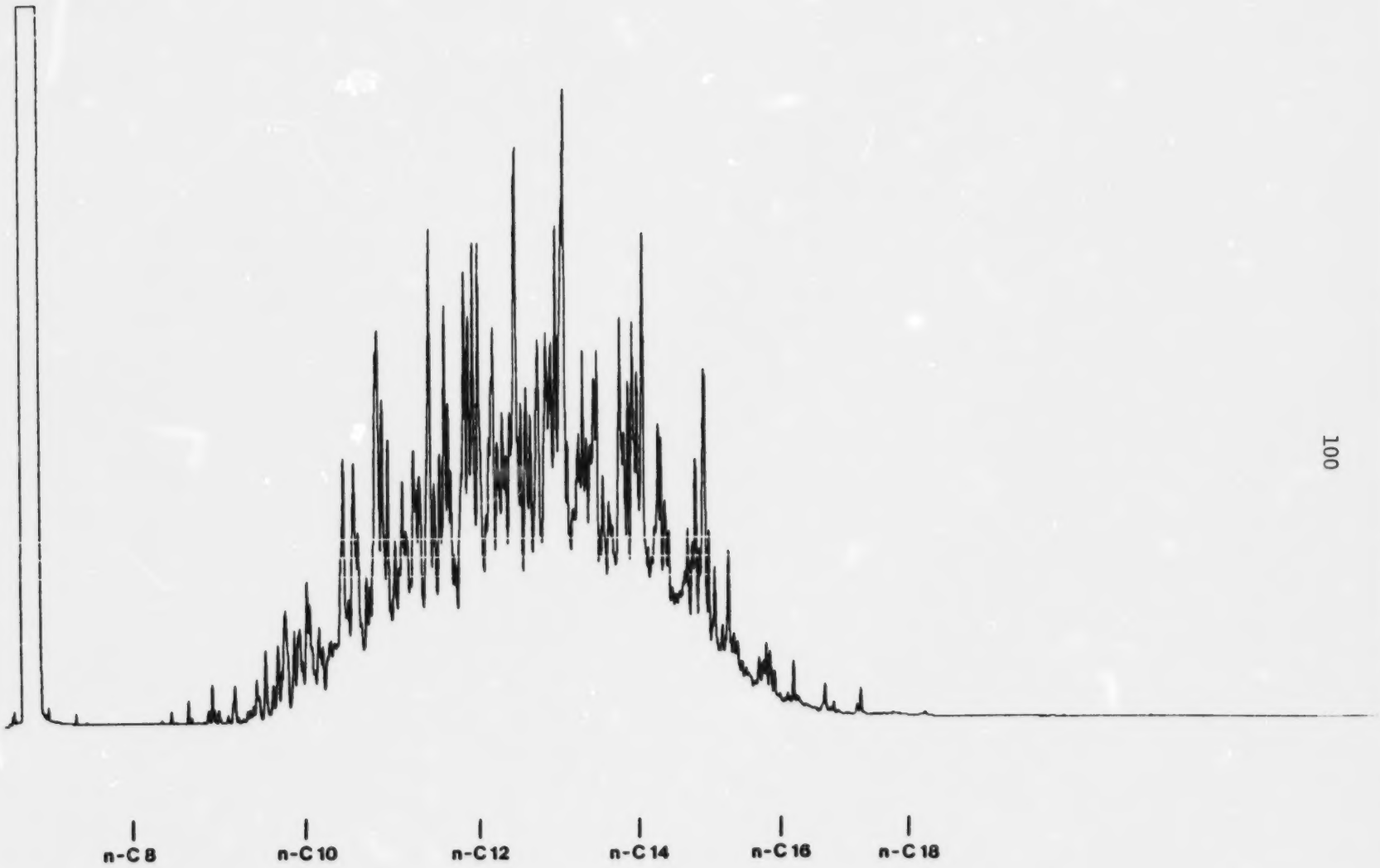
GC trace of the 25 x 10 cm surface sample collected on Day 5 from the wave tank.



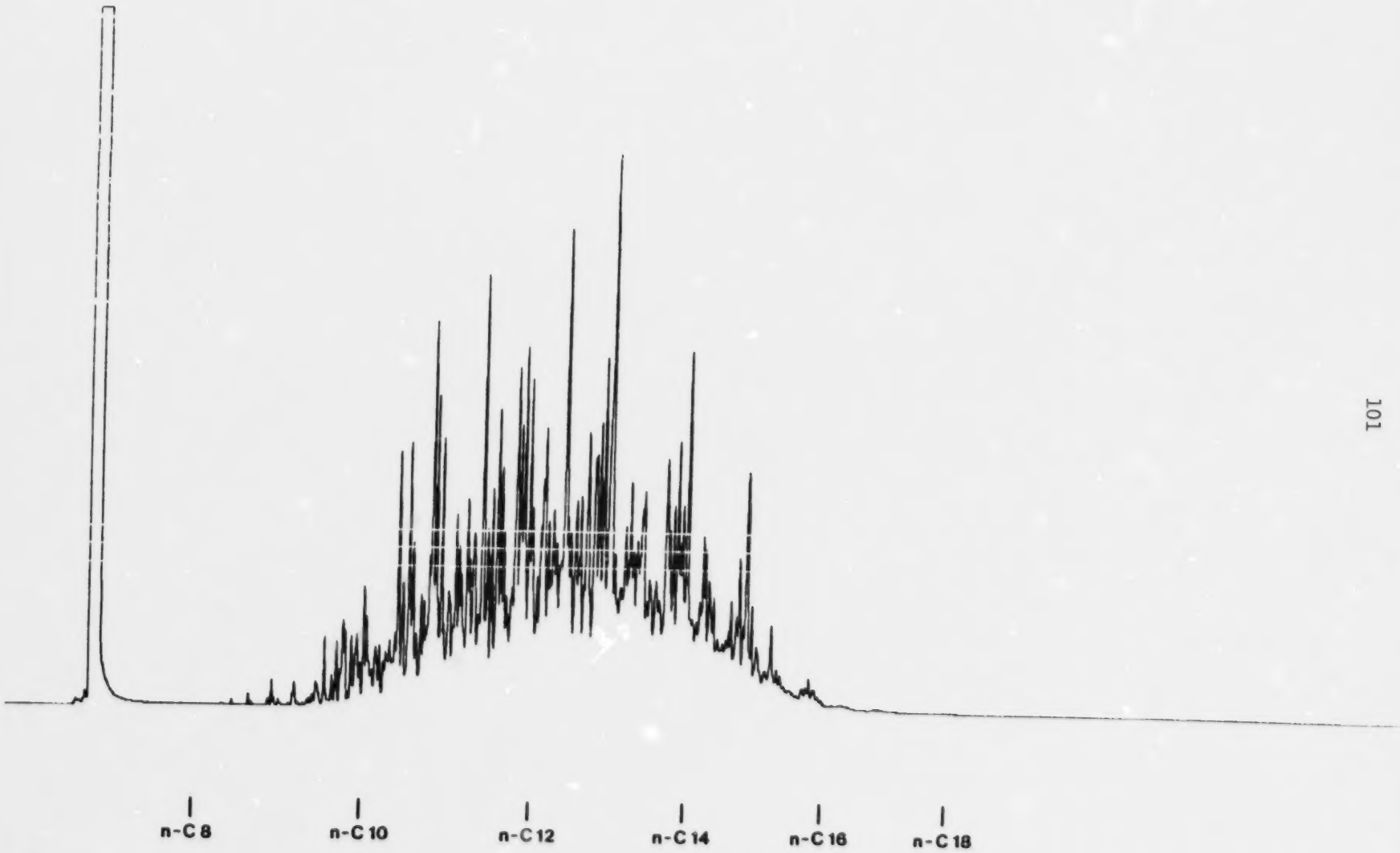
GC trace of the 105 x 30 cm surface sample collected on Day 8 from the wave tank.



GC trace of the 115 x 20 cm surface sample collected on Day 19 from the wave tank.



GC trace of the 35 x 10 cm surface sample collected on Day 26 from the wave tank.



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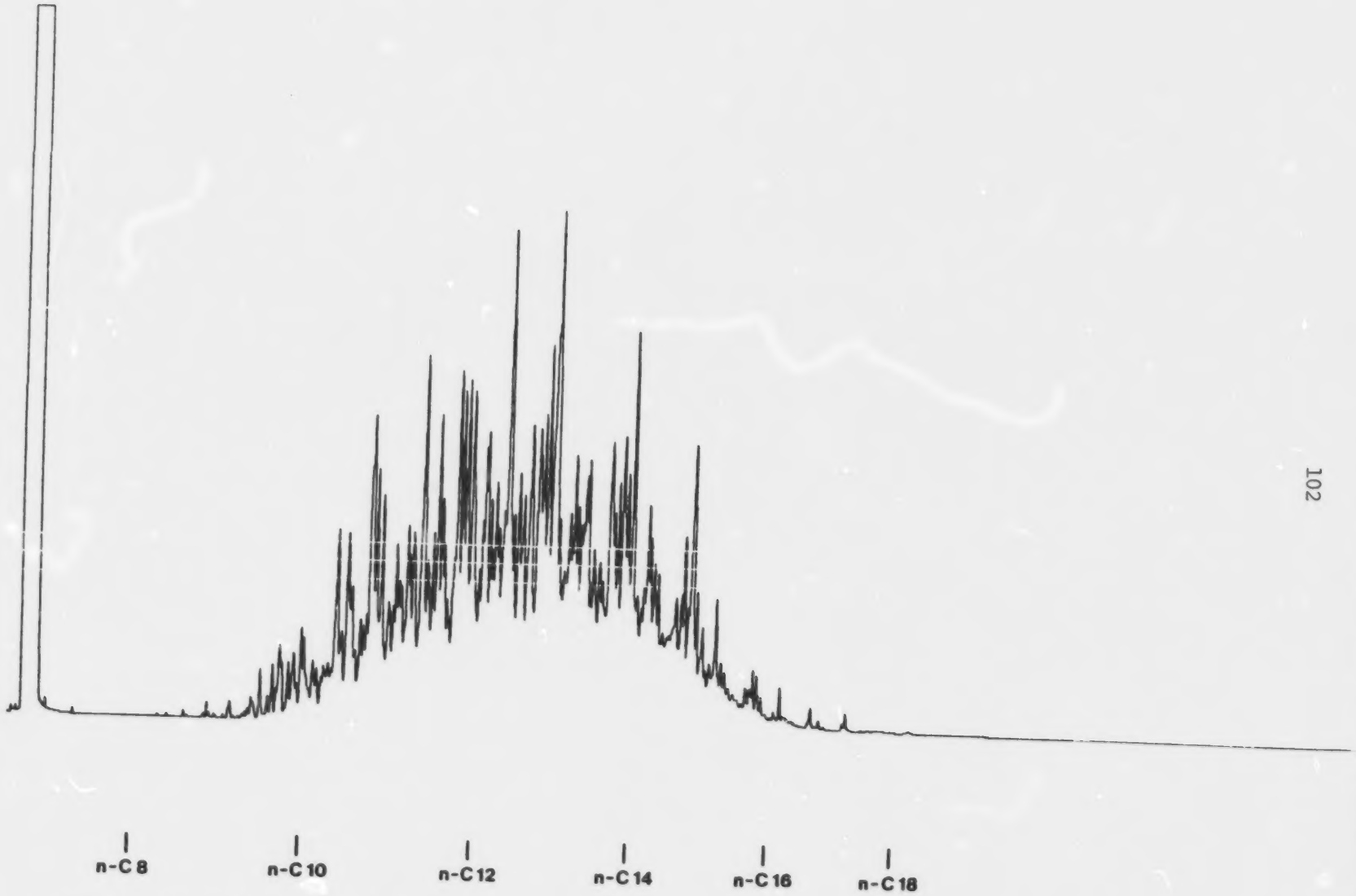
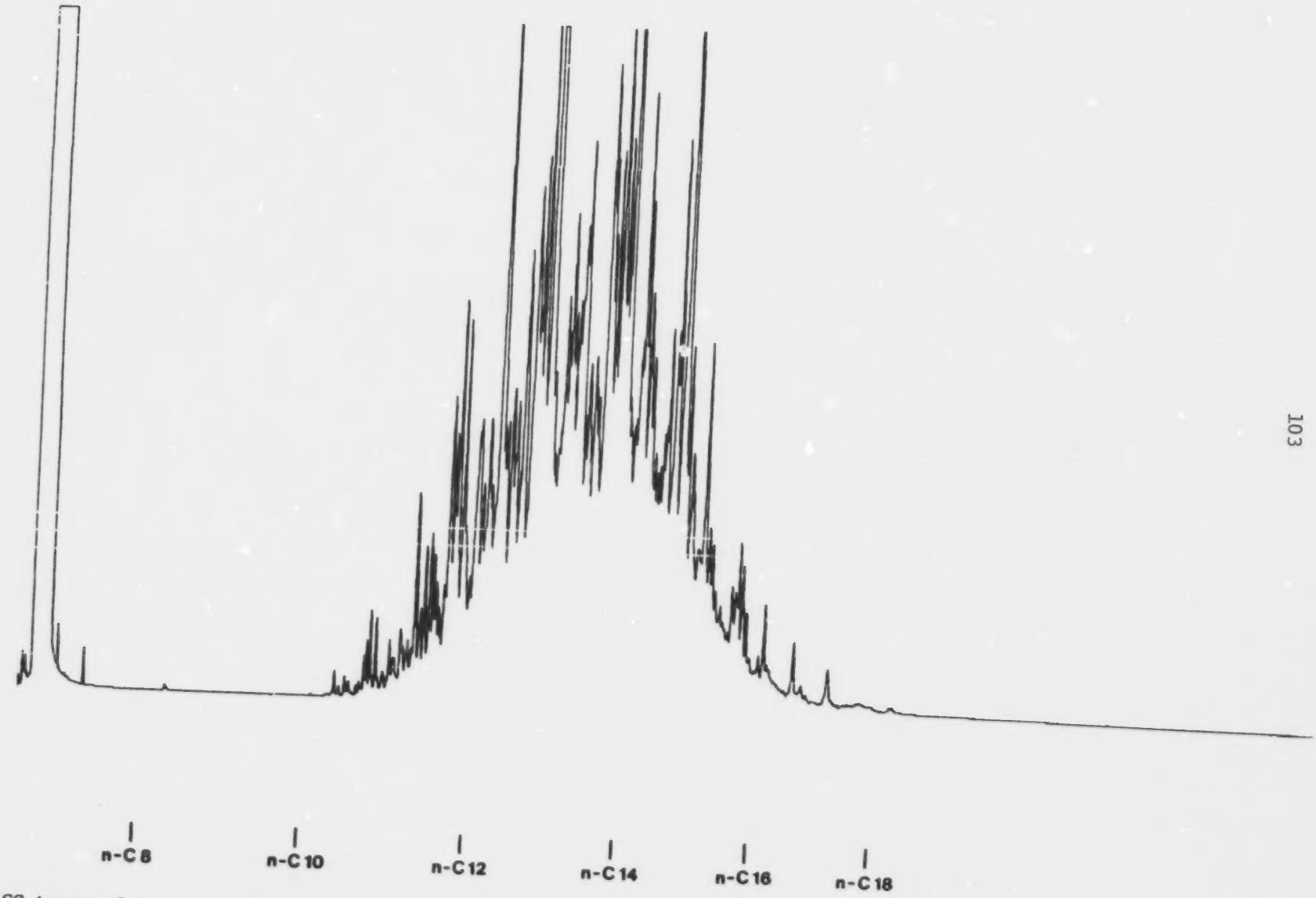
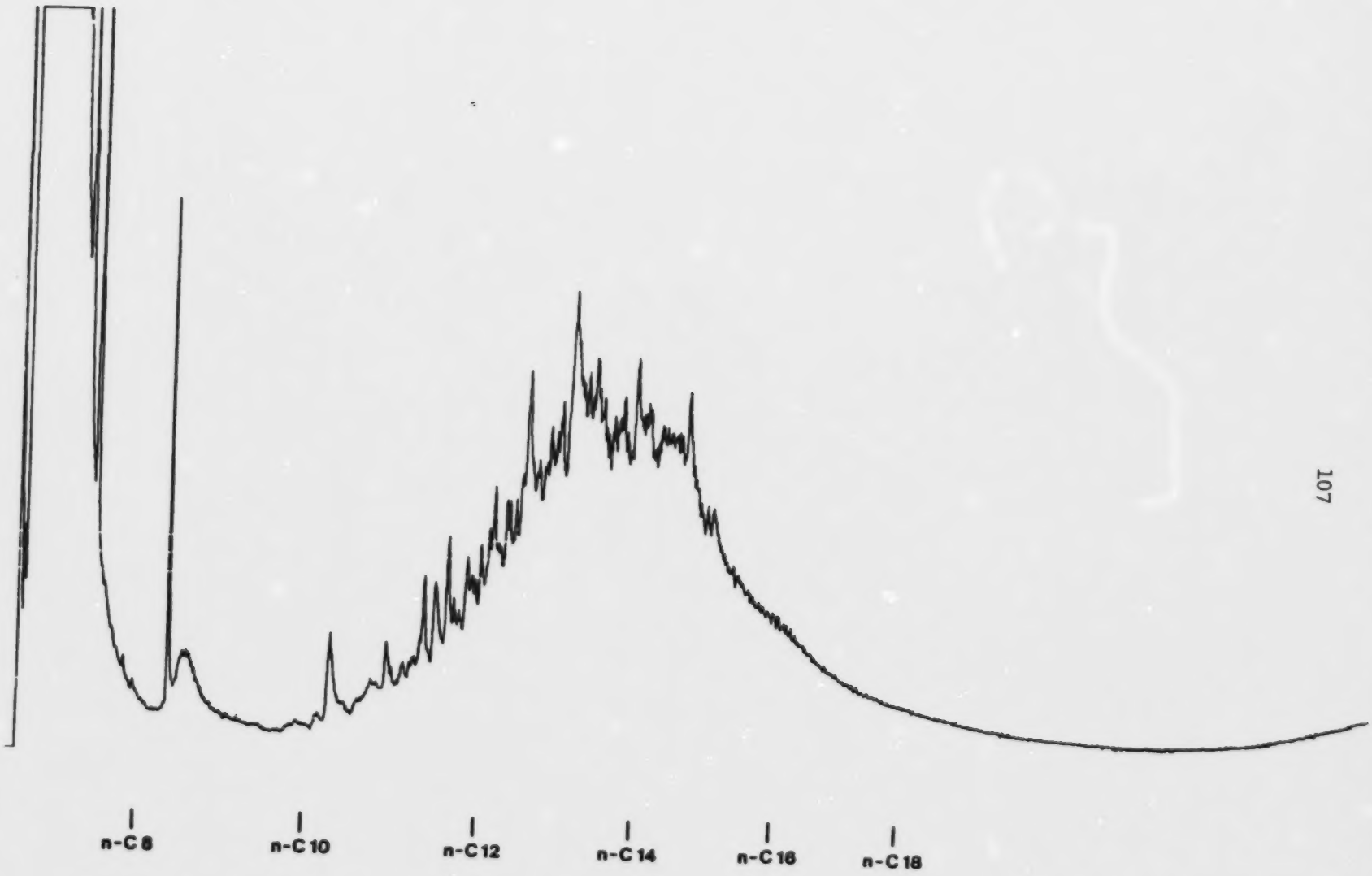


GC trace of the 60 x 15 cm surface sample collected on Day 49 from the wave tank.

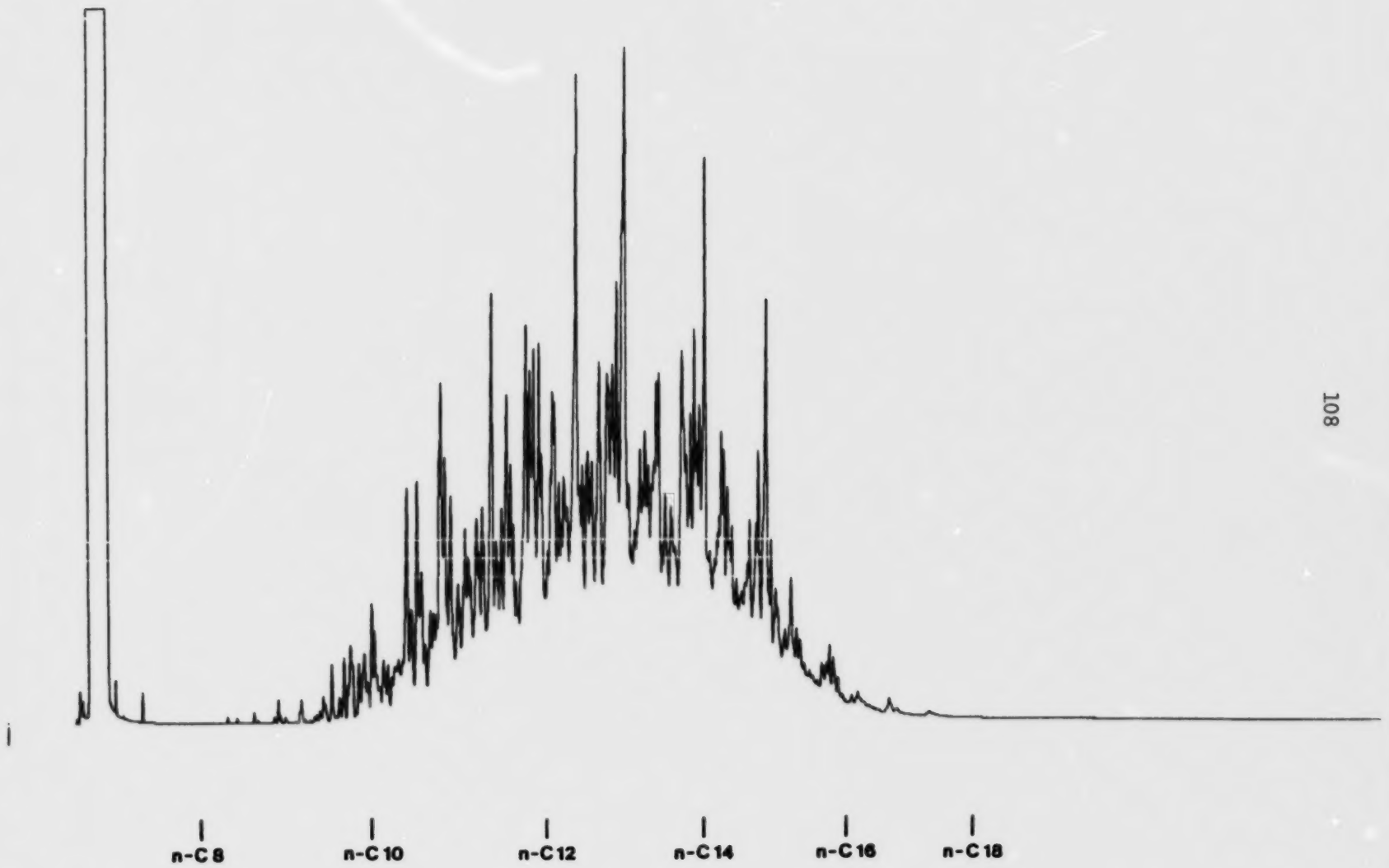


GC trace of the 60 x 15 cm subsurface sample collected on Day 49 from the wave tank.

GC Traces of Water Samples



GC traces of surface water samples collected on Day 8 from the static tank.



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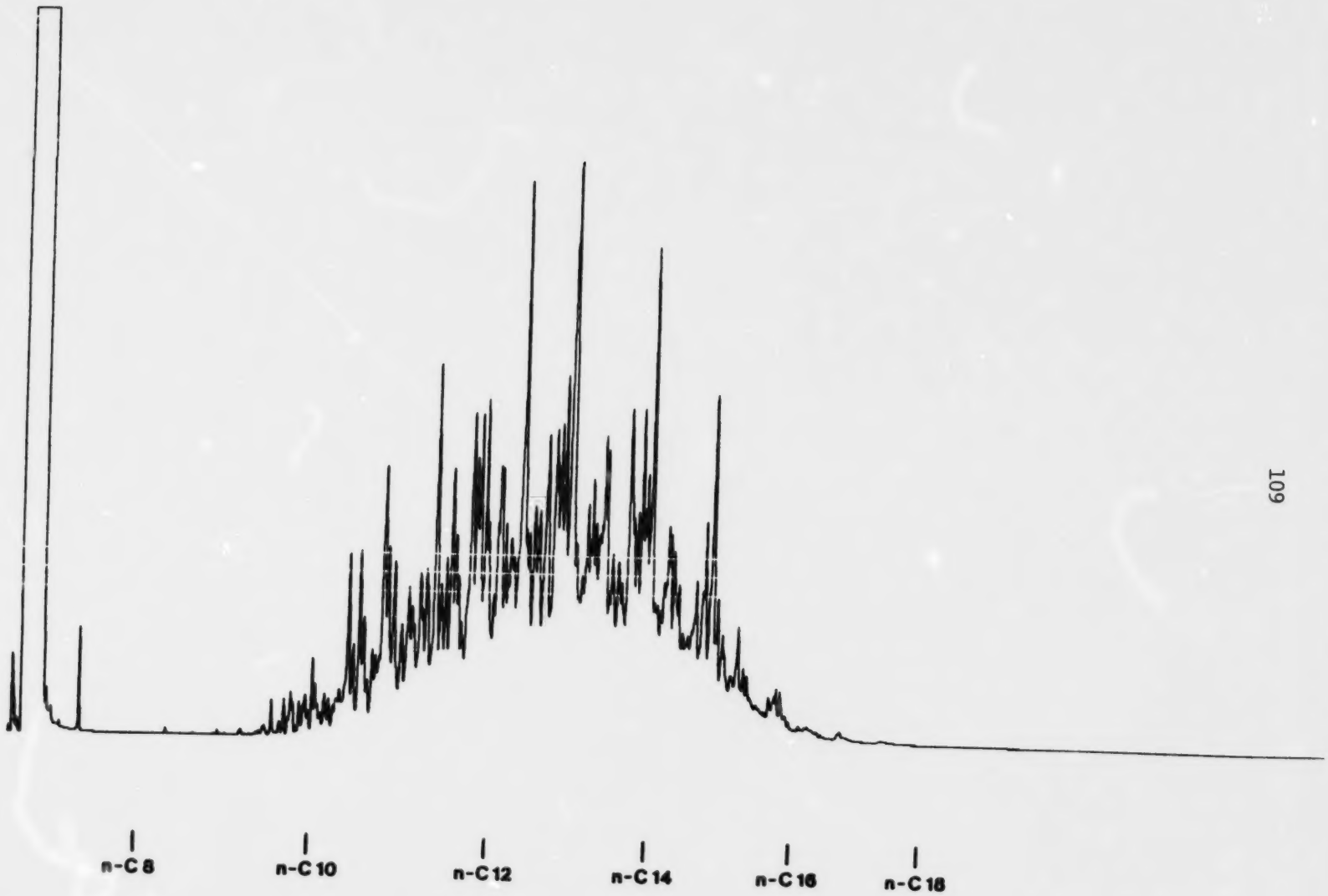

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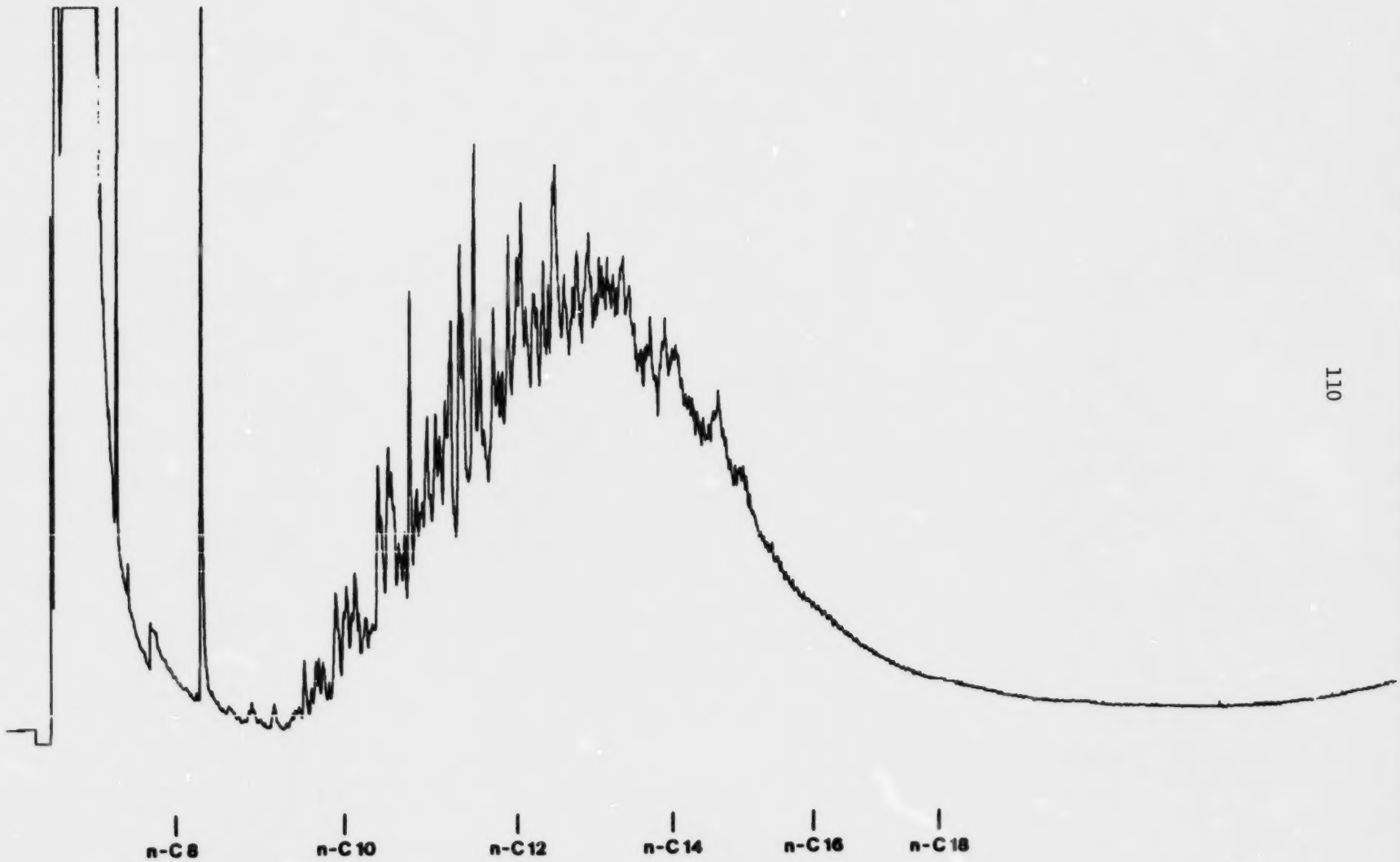

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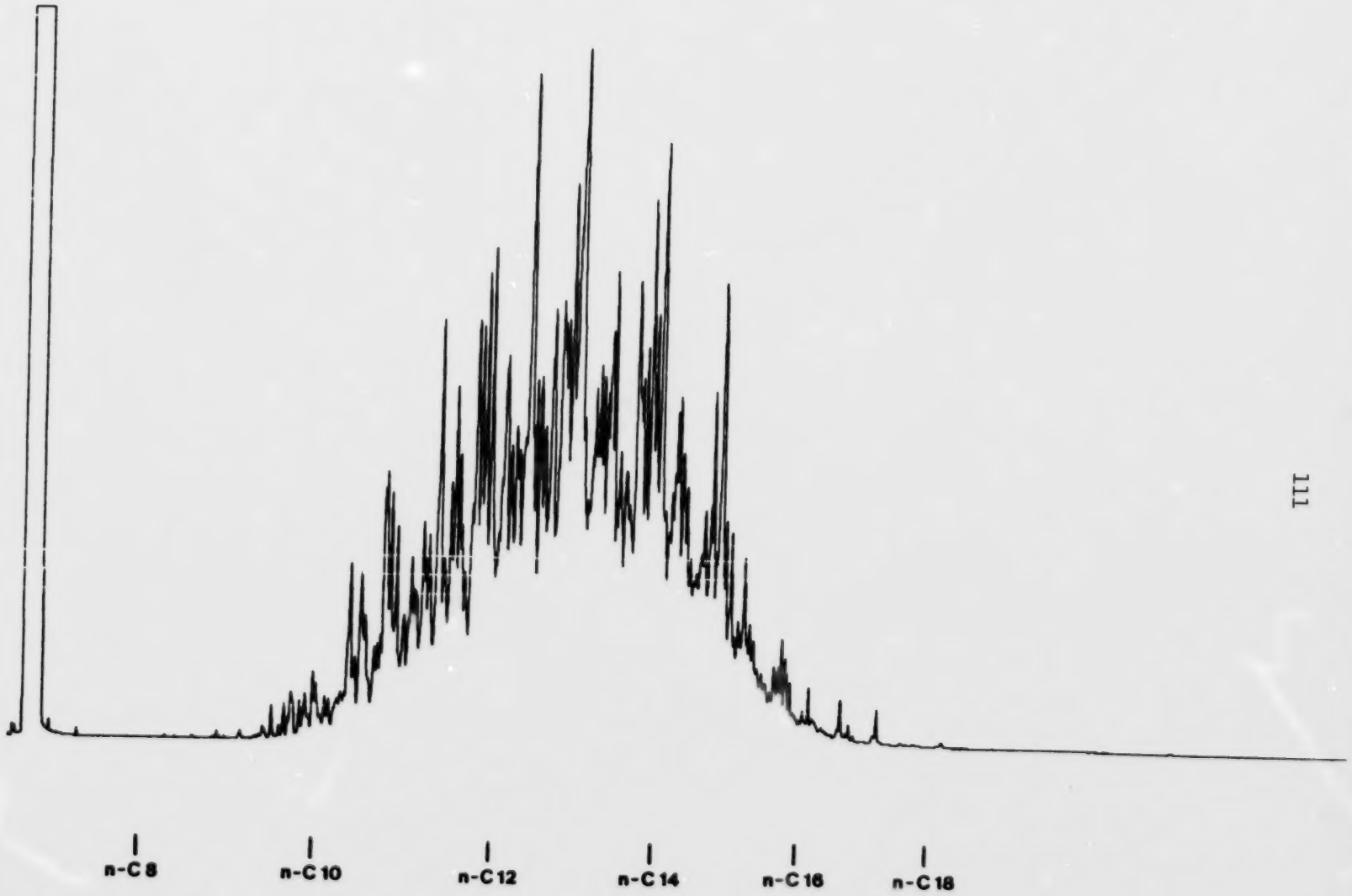

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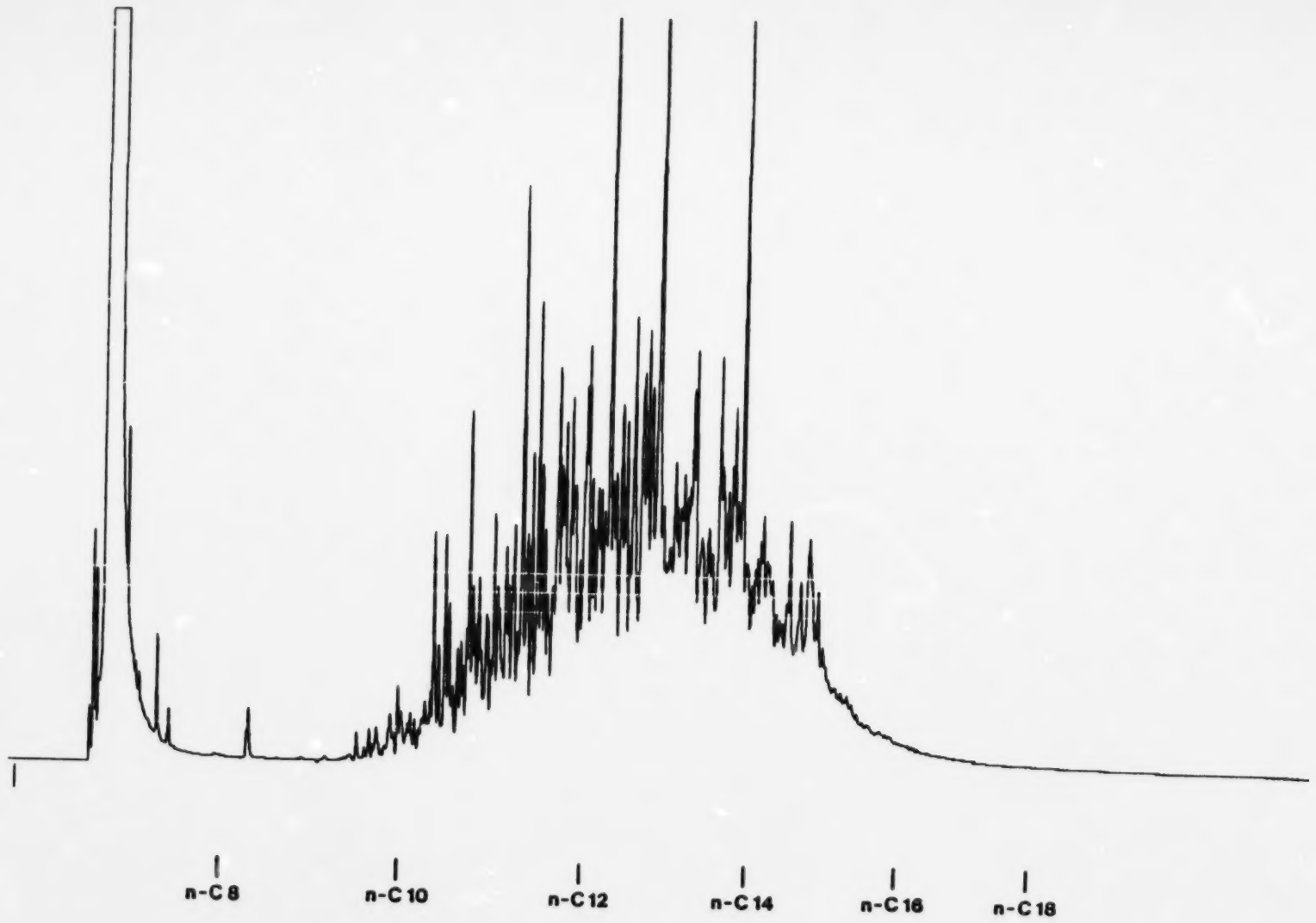

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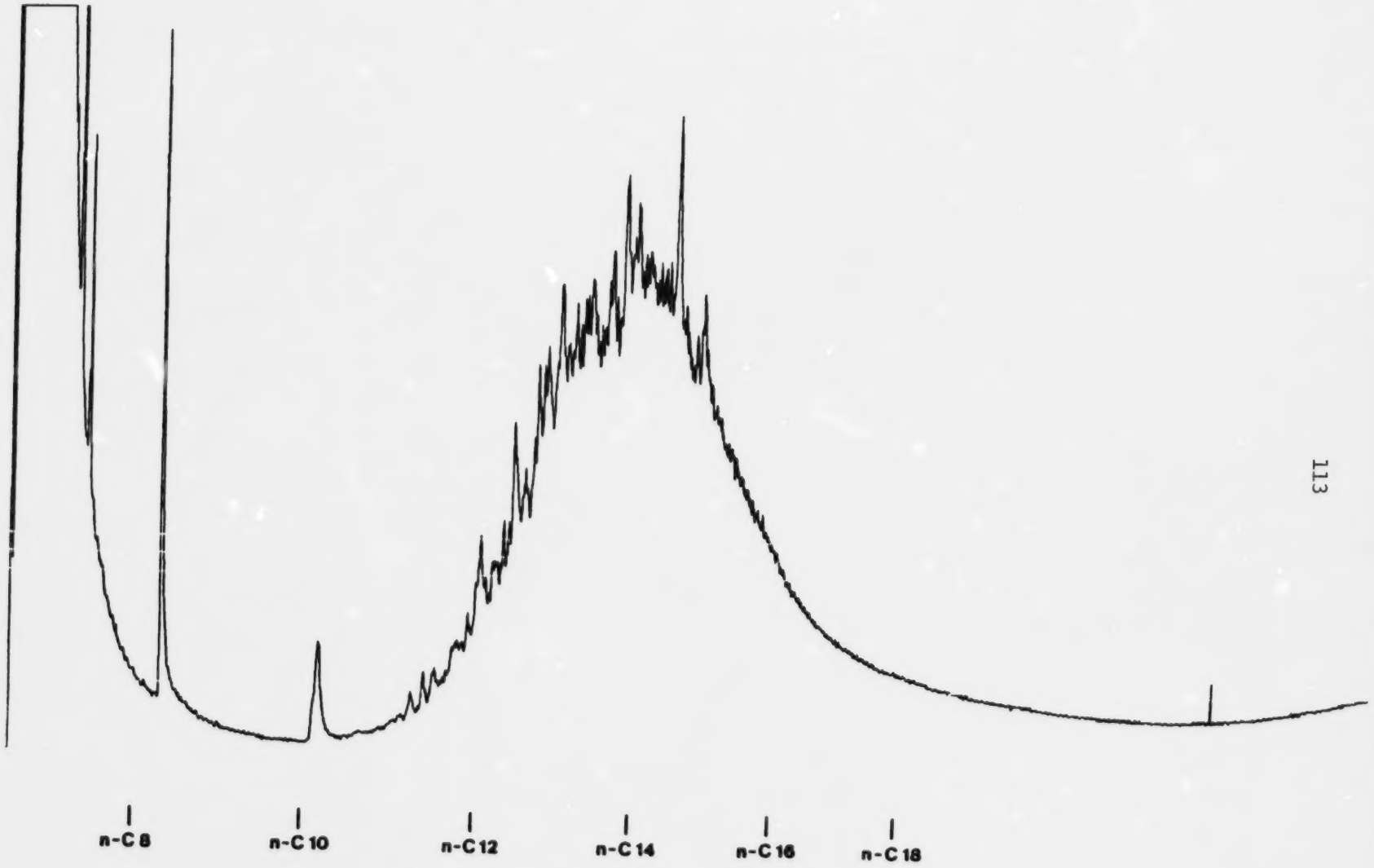

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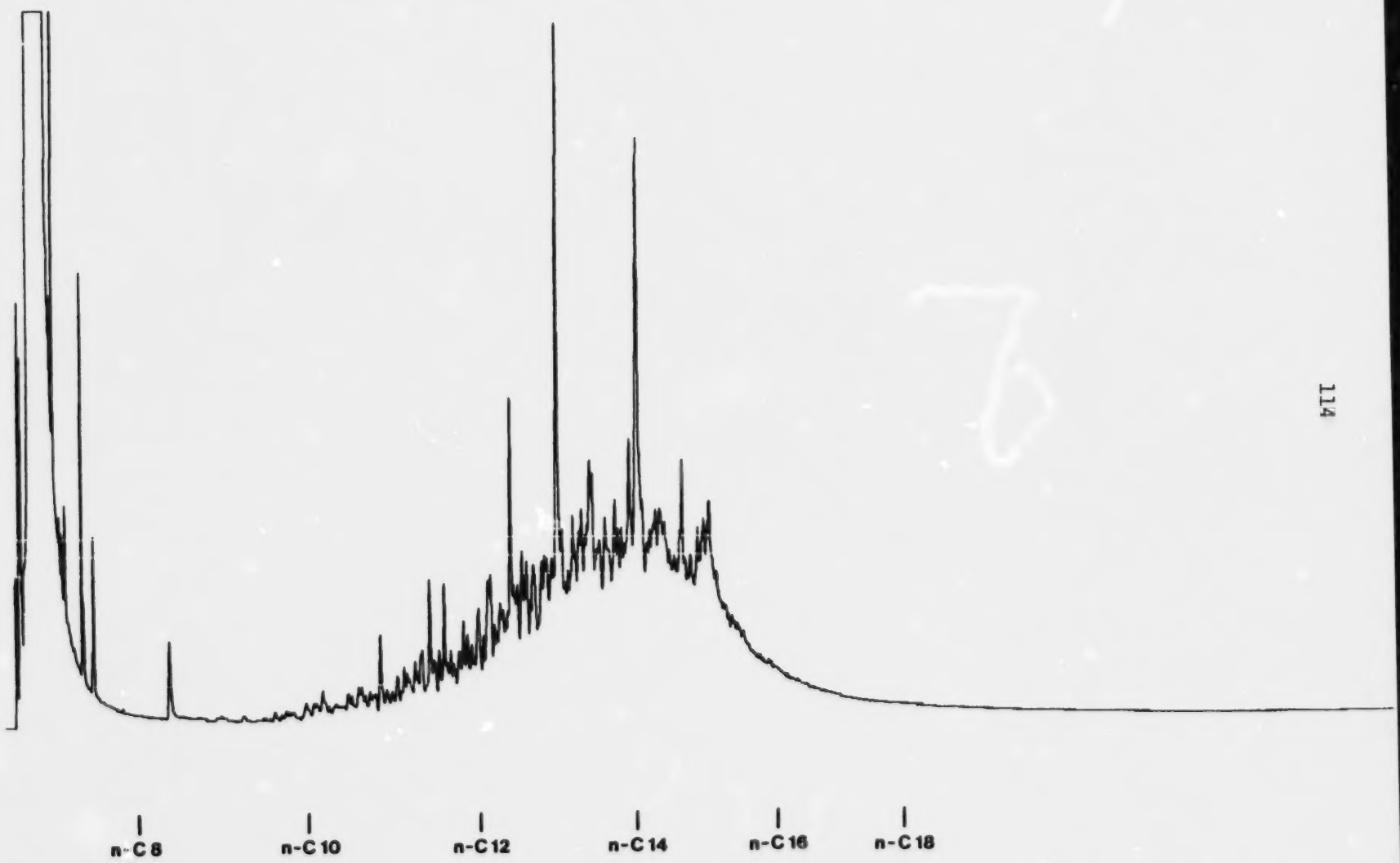

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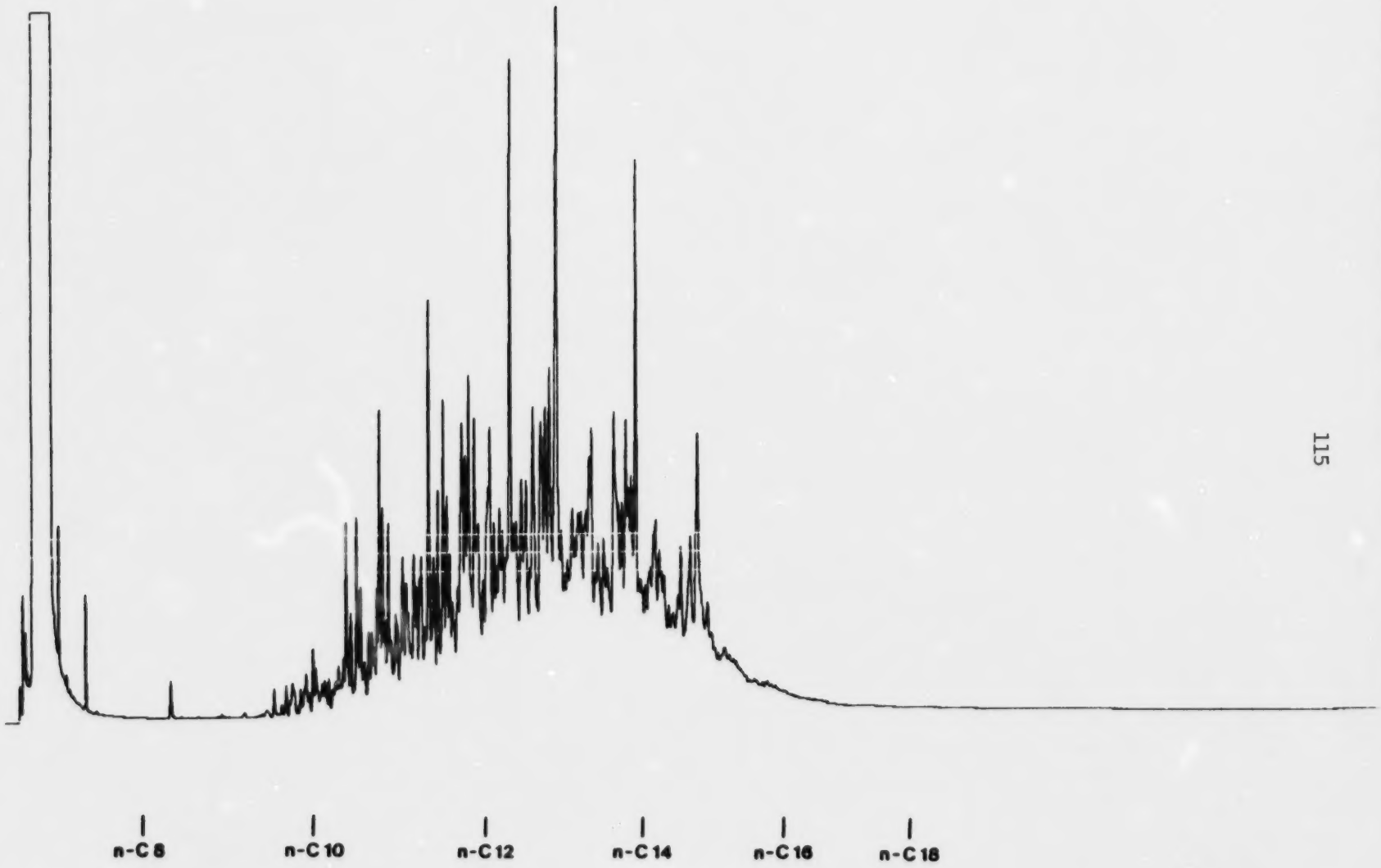

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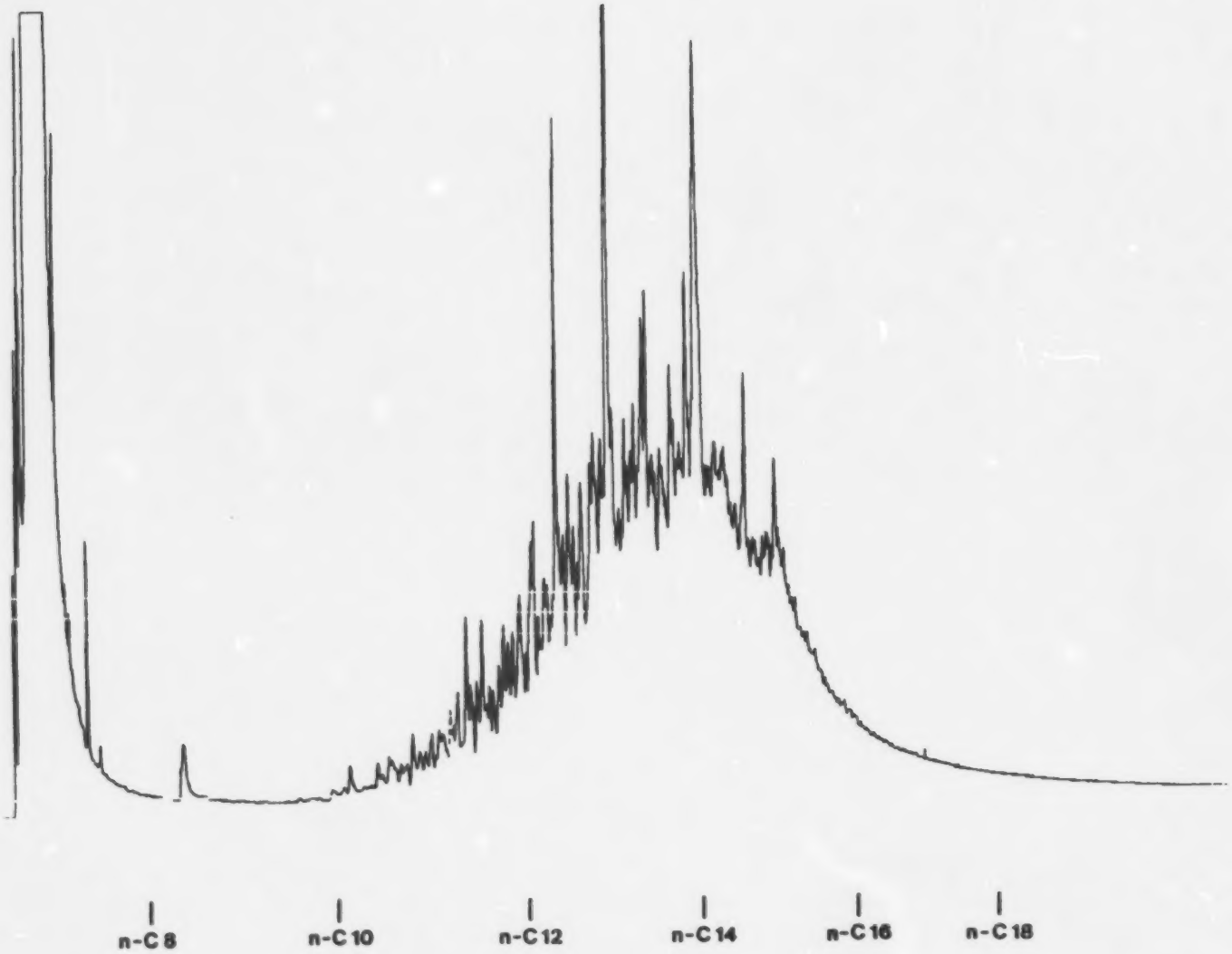

GC traces of surface water samples collected on Day 26 from the wave tank.

OXYGEN DEMAND OF OILED DRILL CUTTINGS
FINAL REPORT

Submitted to:

Indian and Northern Affairs Canada
Arctic Waters Division
Yellowknife, N.W.T.
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ABSTRACT

This report describes a laboratory study of the oxygen demand of oiled drill cuttings layered over natural marine sediments. Treatments and the test temperature were chosen to reflect conditions in the Canadian Arctic where oiled drill cuttings currently pose a solid waste disposal problem. A review of methods for determining the oxygen demand of aquatic sediments was conducted and a core incubation procedure using the micro-Winkler titration method was chosen for use in the experiments. A review of work related to the oxygen demand of oiled sediments was also performed.

The primary emphasis of the study was to determine the total sedimentary oxygen demand at time intervals to 30 days of oiled drill cuttings layered over either coarse (sand) or fine marine sediments in 1, 2.5, 5 and 15 mm thicknesses. Redox potential (Eh) profiles were made through the cuttings and sediment each time oxygen demand was determined. A secondary objective was to determine changes in the pore water concentrations of mercury, copper, cadmium, lead and zinc with time.

Oiled cuttings layered over sediments resulted in up to 18 fold increases in total oxygen demand relative to controls, although two to nine fold increases were the norm. Rates of oxygen consumption ranged from 0 to 19.23 mL O_2 m^{-2} hr^{-1}. Differences in oxygen demand rates were distinguishable after two to four weeks and the rates of fine sediment treatments were usually greater than those of coarse sediment treatments. Oxygen demand was related to time and cuttings layer thickness by the expressions:

A. FOR FINE SEDIMENT

$$O_2 = -3.68 - 0.27\ TIME - 1.60\ \log_{10}(THICKNESS + 0.05)$$

B. FOR COARSE SEDIMENT

$$O_2 = -2.25 - 0.28\ TIME - 2.26\ \log_{10}(THICKNESS + 0.05).$$

where O_2 was in mL O_2 m^{-2} hr^{-1}, TIME in days THICKNESS in mm.

Maximum oxygen demand was observed with a 2.5 mm cuttings layer after 30 days. Thicker layers appeared to mask the activitiy of underlying sediments and had lower oxygen demand rates.

Eh changes in sediments under cuttings were slight, although the largest changes occurred under the thickest layers. Copper concentrations in pore waters of fine grained sediments increased by a factor of 4 over a 30 day period. Levels of Cd, Hg and Pb were unchanged while Zn levels decreased.

RÉSUMÉ

Ce rapport décrit une étude réalisée en laboratoire sur la demande d'oxygène des déblais de forage contaminés par le pétrole, disposés en couches sur des sédiments marins naturels. On a choisi des traitements et une température d'essai qui reflètent les conditions prévalant dans l'Arctique canadien où l'élimination des déblais de forage contaminés constitute actuellement un problème. On a revu les méthodes servant à déterminer la demande d'oxygène des sédiments aquatiques, et on a utilisé dans les expériences une technique d'incubation de carottes faisant appel à la micro-méthode de titrage Winkler. On a également revu les travaux réalisés sur la demande d'oxygène des sédiments contaminés par le pétrole.

L'objectif principal de l'étude était de déterminer à des intervalles pouvant atteindre 30 jours la demande d'oxygène totale de sédiments constitués de déblais de forage contaminés, disposés en couches de 1, 2, 5, 5 et 15 mm d'épaisseur sur des sédiments marins grossiers (sable) ou fins. Chaque mesure de la demande d'oxygène était accompagnée d'une détermination du profil de potentiel rédox (Eh) dans l'ensemble sédiments-déblais. On a aussi déterminé les variations de concentration de mercure, de cuivre, de cadmium, de plomb et de zinc dans l'eau de porosité.

La présence de déblais de forage dans les sédiments entraînait, par rapport à des témoins, une augmentation de la demande d'oxygène totale par un facteur pouvant atteindre 18, même si des augmentations par un facteur allant de deux à neuf étaient normales. La vitesse de consommation d'oxygène variait de 0 à 19,23 mL de O_2 $m^{-2}.h^{-1}$. Les différences de vitesse de consommation d'oxygène devenaient perceptibles après 2-4 semaines; cette vitesse était normalement plus élevée dans les sédiments fins que dans les sédiments grossiers. La demande d'oxygène était reliée au temps et à l'épaisseur des couches de déblais, par les expressions suivantes:

A. POUR LES SÉDIMENTS FINS

$$O_2 = -3,68 - 0,27 \text{ TEMPS} - 1,60 \log_{10} (\text{ÉPAISSEUR} + 0,05)$$

B. POUR LES SÉDIMENTS GROSSIERS

$$O_2 = -2,25 - 0,28 \text{ TEMPS} - 2,26 \log_{10} (\text{ÉPAISSEUR} + 0,05)$$

dans lesquelles O_2 est en mL de O_2 $m^{-2}.h^{-1}$, le TEMPS est en heures et l'ÉPAISSEUR est en mm.

On observait une demande d'oxygène maximale après 30 jours avec des couches de déblais de 2,5 mm. Des couches plus épaisses semblaient masquer l'activité des sédiments sous-jacents, et la demande d'oxygène dans ces couches était plus faible.

Les variations de Eh dans les sédiments sous les déblais étaient faibles, même si les variations les plus importantes étaient observées sous les couches les plus épaisses. La concentration de cuivre dans l'eau de porosité des sédiments fins augmentait par un facteur de quatre sur une période de 30 jours. Les concentrations de Cd, de Hg et et Pb demeuraient inchangées, tandis que les concentrations de Zn diminuaient.

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1.0 INTRODUCTION

The characteristics and environmental concerns associated with the use of low toxicity paraffin oil base muds in Canada have been summarized by Thomas et al. (1983). Among the observed environmental effects where these types of muds have been used are decreases in oxygen content of sediments and near bottom waters after oiled cuttings have been discharged. The most extensive data on oiled cuttings effects comes from field studies in the North Sea summarized in Davies et al. (1984). There are a number of possible mechanisms responsible for some of the effects observed in the field. Oxygen demand induced by bacterial degradation of oil may account for the depletion of oxygen in the water column. When discharged oiled cuttings completely cover the natural bottom sediments, they may form a barrier to the mineral and gaseous exchange processes between the sediments and water. In thinner layers, they may serve as an additional organic substrate for metabolism by benthic microbiota. With complete isolation of underlying sediments from overlying waters, normal chemical and biological oxygen requirements of the sediments are not satisfied and sediments can become anoxic. This process makes the habitat unsuitable for those benthic invertebrates that rely on oxygen for metabolism and alters physico-chemical conditions (pH, Eh, pO_2) sufficiently to permit changes in the chemical states of metals in sediments and cuttings.

The objectives of this study were to review the methods available for determining oxygen demand at the sediment water interface, review any work available on the oxygen demand of oiled cuttings and apply this existing knowledge to an experimental study to test the hypothesis that the oxygen demand of sediments under oiled cuttings layered on the seafloor is the same as that of the natural sediments. The focus of the study was the arctic marine environment. As part of this evaluation, the influences of underlying substrate type (fine or coarse marine sediment) and cuttings thickness were evaluated as independent variables. Additional objectives were to observe the change in the redox potential of cuttings and sediments covered by seawater and test the hypothesis that the pore water concentrations of the metals were the same at the start (day 1), on day 15 and at the end of 30 day flow-through experiments.

2.0 REVIEW OF PROCEDURES FOR DETERMINATION OF OXYGEN DEMAND AT THE SEDIMENT WATER INTERFACE

The oxygen demand of sediments is usually determined in order to provide an indication of metabolic activity in the sedimentary habitat. Oxygen is the terminal electron acceptor in aerobic metabolic pathways and the rate at which it is consumed is an indirect measure of hydrogen production through successive dehydrogenation steps. Other methods mentioned below are available for estimating metabolic activity, however the objective of this study was to assess the magnitude of oxygen demand of sedimentary material (oiled cuttings over natural sediments). This study's goals were to determine the effect this oxygen demand would have on the oxygen content of overlying waters rather than trying to address the processes responsible for the oxygen requirement. The review that follows is therefore presented from this perspective.

The oxygen demand of sedimentary material in aqueous environments has been determined with relatively the same methods for many years (e.g., Baity, 1938). Developments in microelectronics have permitted more technically advanced systems, although they are still based on the same principles. Comprehensive reviews of methods for measuring benthic community metabolism are found in Pamatmat (1977), Zeitzschel (1981), Newrkla (1983), and Patching and Raine (1983).

The oxygen demand of sediments has been determined in situ using enclosures over the sediments and in the laboratory with cores of sediments. Concerns that must be addressed are whether to stir the overlying waters and the appropriate degree of agitation. Other factors to consider are:

- chamber volume versus expected rate of decrease of oxygen concentration;
- exchange rates in flow-through systems versus oxygen consumption rates.

Three primary methods for detecting oxygen concentrations are:

1) chemical titration using modifications (e.g., Fox and Wingfield, 1938; Carritt and Carpenter, 1966) of the Winkler method (Strickland and Parsons, 1972; APHA, 1981);
2) polarographic oxygen probes;
3) gas chromatography.

The first two methods have been the most widely used while the latter requires specialized skills and expensive instrumentation. Gas chromatography has therefore not been routinely implemented (Murray and Grundmanis, 1980; Connor et al., 1982; Howes et al., 1984). GC methods are useful for measuring gas concentrations in headspace over sealed cores and in sediment enclosures.

The Winkler titration is relatively easy to use, can be employed with great precision and can also serve as a calibration method for oxygen probes. However, it provides discrete numbers only and is not practical for obtaining long time series with frequent data points. As a water sample (one to several hundred millilitres) is required for each determination, the volume of water in a closed system is depleted with time unless volumes of water equal to those removed are injected. This method of determination of oxygen concentration is most frequently used when "before" and "after" values are adequate (Smith, 1973; Hartwig, 1978; Bay, 1979; Hinga et al., 1979; van Es, 1982). With skill, the precision of the method can be quite high (± 0.07 mg L^{-1}, Carritt and Carpenter, 1966). Routinely reported precisions range from $\pm 0.5\%$ - 3.0% (Nixon et al., 1976a; Hargrave, 1969a,b).

The applications of polargraphic oxygen sensors (POS) in environmental studies have been recently summarized by Gnaiger and Forstner (1983). Advantages of using POS include the ability to continuously record oxygen concentration over long periods of time and their ease of use. However, POS readings are subject to drift. Some of the reasons for this instability can be eliminated or minimized. A listing of these factors is presented in Table 1. Membrane clogging is most likely to occur in longer term recording situations where films of algae or microorganisms may grow on the membrane. Grease can also clog the membrane and cause a downward drift in POS sensitivity.

TABLE 1

FACTORS CAUSING INSTABILITY OF POLAROGRAPHIC OXYGEN SENSORS
(MODIFIED FROM HALE, 1983a)

General Drift	Osmotic effects (-)
	Release of membrance stress (-)
	Leakage or evaporation of a gross excess of electrolyte (+)
	Membrane erosion (+)
	Membrane clogging (-)
Short-term Fluctuations	Flow rate variations of sample
	Orientational (gravitational) effects
	Applied pressure effects

When choosing a POS, a compromise must be reached between stability, speed of response, residual current and stirring requirements (Hale, 1983a). A low permeability membrane is most appropriate when stable, long-term monitoring is desired. This type of membrane is less sensitive to stirring rate. The trade-off is decreased sensitivity to short-term fluctuations in oxygen concentrations. For situations where a rapid response is required, higher permeability membranes should be used, with their concomitant greater stirring requirements and need for frequent recalibration. The accuracy of POS is in the range of ±0.02 to 0.03 mg L^{-1} for YSI and Orbisphere Laboratories products (manufacturer's literature). Reported values range from ±0.01 to 0.1 mg L^{-1} (Smith et al., 1976; Hargrave and Connolly, 1978; Hargrave et al., 1983).

Electrodes are rapidly poisoned by dissolved hydrogen sulfide (Fenchel, 1969, Hale, 1983b). POS that are insensitive to H_2S are commercially available (Orbisphere Laboratories) for such situations.

Common problems that may occur under experimental conditions include oxygen diffusion through substances such as perspex enclosure walls or teflon tubes. The magnitude of the flux is gradient dependent and is therefore of most concern when oxygen concentrations are low in the measurement chamber and high in the surrounding water.

Two other methods for determining the metabolic activity of sediments involve the use of dehydrogenase enzymes to measure the rate of hydrogen or electron transfer and direct calorimetry to measure heat production. Reduction of TTC(2,3,5-tri-phenyltetrazolium chloride) to formazin has been used for the first type of measurements (see review by Pamatmat, 1977). The shortcoming of these enzymatic types of assays is that the numbers cannot readily be equated to measures of metabolic state (Parsons et al., 1984), however they may be useful for comparative purposes (Pamatmat, 1977). Calorimetry suffers from an inability to discriminate between metabolic heat production and enthalpy changes. Neither method was suitable for fulfilling this project's objectives.

3.0 REVIEW OF STUDIES RELATED TO OXYGEN DEMAND OF OILED DRILL CUTTINGS

The present knowledge of the environmental fate and effects of oiled drill cuttings is most extensive for the North Sea and has been most completely summarized by Davies et al. (1984). Oxygen demand that may be associated with oiled cuttings was not specifically addressed, however the chemical changes that occured in underlying sediments once cuttings were deposited on them in the field were mentioned. One of the changes was decreases in the oxygen content of sediments as inferred from redox potential decreases (Eh). Most of the measurements have been part of field monitoring programs. This brief overview is restricted to studies that have, or are addressing the oxygen demand of oiled cuttings.

Three studies are considered relevant to this review. None of the results were available in printed form and the information that follows is derived from conversations with the principal investigators of each project. A list of these sources is provided in Appendix A. The information should therefore be regarded as preliminary and subject to revision in print.

The Oil Pollution Research Unit in Pembroke, Wales recently completed field trials with oiled plots in Milford Haven (B. Dicks, pers. comm.). Eighteen replicate plots and controls were set up in 15 m of water and left for approximately one year. They were oiled with cuttings containing different types of mineral oils. Two application levels were used: 1) 1000 to 5000 ppm oil; and 2) 100 to 500 ppm oil. Davies et al. (1984) had defined zones of chemical and biological influence away from oiled cuttings discharge sites. One zone closest to the discharge had peak densities of opportunistic fauna. Further away, less biological disturbance was evident and oil concentrations were lower. The application levels were chosen to represent the oil concentrations that prevail within these two zones around North Sea oil platforms. For heavy applications, natural sediments were mixed with cuttings by first sun drying the natural sediments to sterilize them, mixing the cuttings with the sediments and then applying the mixture over natural sediments. If mixing was too vigorous, a hard

concrete like sheet tended to form on the surface. They did not measure oxygen demand of these treatments per se, but did determine how oil degraded with time as a result of chemical and biological weathering processes. Rather fast rates of loss of oil were observed. With the treatments that they used, they judged that recovery rather than degradation of the bottom sedimentary habitats was being observed. Little erosion occurred in the sheltered area where the experiments were conducted.

A recently completed doctoral thesis (K. Dow) project at the University of Aberdeen looked at the fate of oil and effects of oiled cuttings on bottom sediments in tank experiments (K. Dow and J.M. Davies, pers. comm.). The project objectives were to determine the effects of oiled cuttings on microbial populations and their effect in turn on the chemical characteristics of the sedimentary environment. Approximately 18, 1.5 m diameter tanks were set up with two concentrations of cuttings. Low organic content natural sediments were used with cuttings containing diesel oil or an early generation mineraltype oil, Cleanspot. The residual oil content on the cuttings was approximately 13%. A low density application of cuttings was intended to represent cuttings concentrations approximately 500 m from drilling platforms (Davies et al., 1984). A high density application had about 5 to 10 mm of cuttings overlying the natural sediments. This application represented about 6 kg of cuttings throughout the tank. The experiment ran for approximately 18 months. Eh profiles, organic carbon content, nitrogen and sulfate content of the sediments were determined at intervals throughout the experiments. Respiratory demand of the cuttings was also determined at these times. Treatments were run in triplicate and redox profiles were taken at three positions within each tank.

Eh profiles were the same in the high application level tanks, but the profiles in the low application tanks were dependent upon whether the measurements were taken near a concentration of cuttings or not. Categories were defined for the amount of cuttings in these low application experiments and the changes in redox potential were related to the categories.

Cuttings were applied by several methods. The first method consisted of putting the cuttings in a garden sieve and applying what came through

to the experimental tanks. A better method involved the preparation of a slurry of cuttings and seawater which was then pumped into the tanks. This method permitted more even application of the cuttings layer over the sediment surface.

Oxygen consumption determinations were made in closed cores pushed into the sediments in the test tanks. Incubation times of up to twelve hours were used. Specific data were not provided by the investigators, but they did indicate that there wasn't a notable increase in the oxygen demand of the sediments when cuttings were present. Greater oxygen demand values occurred in the low oil input treatments than in the high. This result may have represented metabolic enhancement as a result of the organic enrichment by the hydrocarbons. Some of the problems encountered were those common to any study involving oxygen electrodes; i.e., drift with time. An Orbisphere Corporation oxygen probe was used which is insensitive to hydrogen sulfide. Cuttings were resuspended if the stirring rates in the cores were too vigorous, and some oil fouling of the probe membrane did occur.

The Norwegian Water Research Institute has recently performed two sets of relevant experiments (T. Bakke, pers. comm.). One set of experiments involved enclosures at 10 m in Oslo Fjord and the other set was a laboratory study. In the first set, thin cuttings layers (approx. 0.5 mm) were applied over 3 m^2 of natural sediment. A fine and a coarse natural sediment were tested. Two types of oiled cuttings were tested: a diesel and a first generation low aromatic mineral-type oil. Cuttings and seawater were mixed vigorously to form a slurry which was pumped to the bottom and spread over the plots.

At time intervals after the start of the experiments, <u>in situ</u> bell jar respirometers were placed on the bottom to record the oxygen demand of the sediments over a 24 hour period. Polarographic oxygen probes were used to record oxygen concentrations in the jars. Data have not been processed at this time.

The laboratory experiments looked at recolonization on cuttings layers

and the fluxes of metals and petroleum hydrocarbons from the cuttings at constant oxygen partial pressures. One half to ten mm layers of cuttings were placed over a base layer of natural sediments in 1 m^2 boxes. Cuttings-sea water slurries (approximately 40% water) were prepared and spread out mechanically over the sediment surface. This technique was suitable for layers as thin as 5 mm. Thinner layers had to be prepared by premixing the slurry with the natural sediments and then laying it down manually. Four types of cuttings were used.

Eh profiles and measurements of the release of petroleum hydrocarbons and metals were performed at specific intervals. No measurements of oxygen demand were undertaken. Sediments under 5 and 10 mm cuttings layers became anoxic very quickly after the start of the experiments. The Eh profiles for the 0.5 and 1 mm cuttings layers were similar to the control profiles. The flux rates of metals (Cu, Ni, Cd, Pb plus several others) were so low after one and three months that measurements were discontinued.

No work on the oxygen demand of oiled cuttings in the United States has been identified. Studies in the U.S. Environmental Protection Agency have concentrated on toxicities of drilling muds and their additives (T. Duke and S. de Nagy, pers. comm.). The use of oil-base drilling fluids in the United States has been restricted and there has not been any field experience with them.

4.0 EXPERIMENTAL MATERIALS AND METHODS

4.1 Test Material

The cuttings used for the study were from the Shell Alma F-67 well drilled on the Scotian Shelf off eastern Canada in 1984. The drilling fluid used in the well contained Conoco mineral oil. A full description of the characteristics of these cuttings was provided in Hutcheson et al. (1984). The cuttings had a total oil content of 8.4%. Cuttings taken from the well in 1984 had been stored for approximately one year in a cold room at 4°C in sealed polyethylene containers. The composition of non-polar hydrocarbons in this sample and a stored solvent extract of the original cuttings were determined by the methods given in Hutcheson et al. (1984).

The grain size distribution in sediments and cuttings was determined by dry sieving and pipette analysis (Walton, 1978). The total organic carbon content was determined according to Pocklington and Morash (1979).

Each sediment was washed with freshwater in the laboratory and dried at 105°C for 12 hours before use. This procedure was undertaken to remove the biological component of sediment respiration and hence increase the ability to detect any oxygen demand due to the oiled cuttings.

4.2 Oxygen Measurement Method

A trial experiment was performed to compare the accuracy of a polarographic oxygen sensor (Yellowsprings Instrument Company Dissolved Oxygen Meter Model 58 and Probe Model 5720A) with values determined by micro-Winkler titration modified for 50 mL water samples.

The titration method was adapted from Strickland and Parsons (1972) and is presented in outline form in Appendix B. Water samples were withdrawn into calibrated 50 mL disposable plastic syringes. The precision of the volume calibration was 0.07% standard error of the mean (S.E.M.). The

precision of the oxygen determinations with the syringes was 0.08% standard error of the mean (n=4) with replicate aerated water samples in the laboratory and in experimental practice was usually ≤0.5% S.E.M.

The experimental treatments consisted of a sediment control, cuttings, and a seawater control. For the sediment control, 25 mL of cleaned sand was added to each of three 125 mL Erlenmeyer flasks. Twenty five milliliters of cuttings were added to each of 11 similar flasks for the cuttings treatment. Flasks were filled with seawater. Nine seawater control flasks were run. The oxygen concentration was then determined in three of the control flasks. An oxygen probe was inserted through a rubber stopper into one of the cuttings flasks with care taken to exclude any air bubbles. The oxygen probe calibration setting was then set to the mean value determined with the titrations of the replicates. All flasks were then stoppered and incubated at 1°C. The oxygen concentrations in the probe flask and the other flasks were determined on days 2, 5, and 8.

4.3 Experimental Design

4.3.1 Preliminary Assessment of Oxygen Demand of Cuttings

In order to most closely simulate conditions on the seafloor, layering cuttings of various thicknesses over natural sediments was chosen for the cuttings application method. Oxygen demand of sediments was to be determined with capped cores driven into the sediments. An initial trial was performed to determine the sensitivity of the oxygen measurement method to detect changes in the oxygen concentrations in closed cores due to the enclosed cuttings over sediment. The intended thicknesses in experimental tanks were: 15, 5, 2.5 and 1.0 mm. With cuttings surface areas of 35.29 cm^2 covered by core tubes to be used for oxygen uptake determinations, the volumes of cuttings enclosed by the tubes for each layer thickness were calculated. These volumes of cuttings that would be enclosed by the core tubes were weighed out in triplicate and added to Erlenmeyer flasks. Flask sizes for the respective layer thicknesses were 125, 50, 50, and 50 mL. The flasks were then vigorously shaken and allowed to stand unstoppered

in a water bath at 2°C for two days. The water was then siphoned off, replaced with water of a known dissolved oxygen concentration, stoppered and left for 24 hours. Triplicate seawater control flasks were also run. The oxygen concentrations in the flasks were again determined.

4.3.2 Oxygen Demand Experiments

The objective of the experiment was to determine if cuttings layer depth, underlying sediment type and time after layering had any significant effects on the oxygen demand of sedimentary material. A 5x2x5 factorial fixed effects experimental design was used with replication. The hypothesis tested was that the population means for each treatment were equal (i.e., Ho: $u_{depth} = u_{thickness} = u_{time}$) versus the alternative hypothesis that they were unequal.

Experiments to determine the oxygen demand of oiled cuttings layered over natural sediments were performed over 30 days in the flow-through mode in 36L capacity glass aquaria (Figure 1). Experiments were run at 1 to 3°C with Bedford Basin seawater at a salinity of approximately 28 to 30 °/oo.

Experimental treatments consisted of 5 cuttings thicknesses:

15, 5, 2.5, 1, and 0 mm.

These were placed over 3 cm layers of both the fine and coarse control sediments on the bottoms of the tanks to give 10 treatment combinations. The control sediments were introduced into empty aquaria, wetted with seawater, mixed and evened out. The cuttings were applied to this surface by first making a slurry of the cuttings in seawater. These two ingredients were mixed 60%:40% (v:v) in a paint can on a paint shaker for ten minutes. The volume of cuttings in the can was measured out to equal the volume required to cover the sediment surfaces with the appropriate thicknesses of cuttings. The slurry was poured over the wetted surface of the control sediments and evened out to a uniform thickness. Seawater was then added

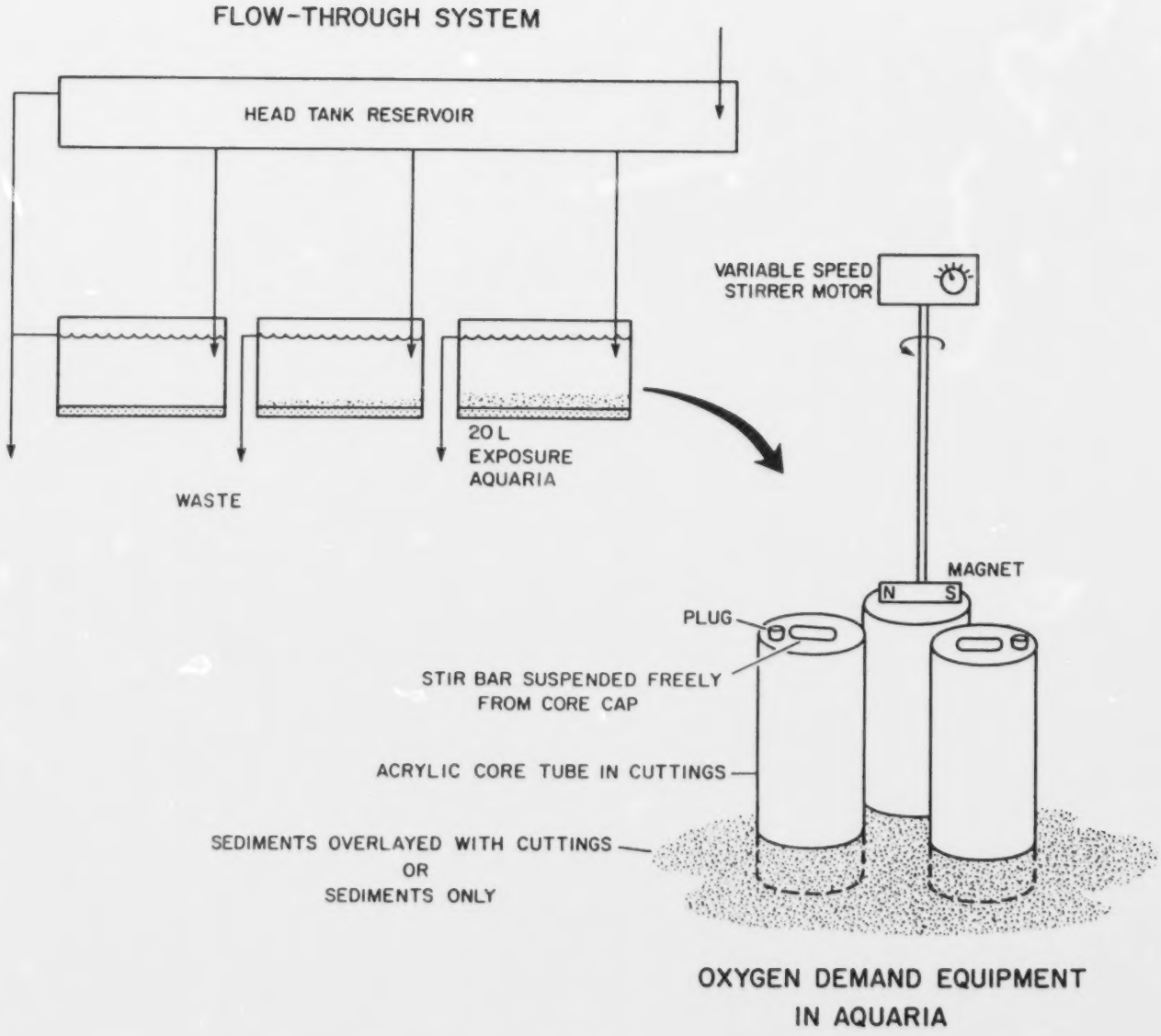

Figure 1. Experimental set-up for oxygen demand determinations.

to the tanks and allowed to flow overnight before any initial measurements were taken.

Aquaria were kept in a temperature controlled water bath. Temperature regulated, sand-filtered seawater was directed into each tank from a head tank at 200 mL min^{-1}. An overflow drain on each aquarium kept about 20-25L of seawater in the tank.

Preliminary trials to evaluate the comparative advantages of a polarographic oxygen electrode over chemical titration as a routine oxygen determination method for these experiments indicated that the probe would be susceptible to fouling by oil. The micro-Winkler titration was therefore employed as the oxygen measurement method. For these measurements, 30 mL samples were taken and analyzed. pH was measured with a Corning pH/Temperature Meter Model 4 and calomel combination electrode (Corning Model 476182). Temperature was determined with either a thermometer or thermistor attached to a YSI Model 33 SCT meter probe. This instrument was also used for measuring salinity of the seawater.

The oxygen demands of the substrates in the tanks were determined on days 1, 3, 7, 15, and 30 by inserting 10 cm sections of 6.75 cm diameter acrylic tubing into the sediments. The tops of the core tubes were capped. There was an access port through the top and a magnetic stir bar was suspended from the cap. Triplicate cores were placed in a cluster in each replicate treatment tank when measurements were to be taken (Figure 1). The sediment surface was never disturbed twice. After the cores were in place in a tank, the tubes were stoppered and the stir bars were rotated slowly with a ceramic magnet suspended above the cluster and attached to the drive shaft of a variable speed motor. At the same time, water from the test tank was collected in a 300 mL BOD bottle which was stoppered and incubated as a control in parallel with the cores. After approximately 24 hours, the water level in the tank was lowered to below the tops of the core tubes. The tubes were unstoppered and up to three replicate water samples of 30 mL each were taken by syringe for dissolved oxygen concentration determination.

Measurements each time an oxygen demand determination was started included dissolved oxygen concentration of the tank water at the time the cores were sealed (C1), pH, temperature, salinity and the redox potential profile through the cuttings and sediment. After an incubation period, dissolved oxygen concentrations in the cores (C2) and BOD bottle (C3), water pH and temperature were recorded.

4.3.3 Oxygen Consumption Rates

Oxygen consumption rates of sedimentary material within the cores were calculated according to the following formula:

$$mL\ O_2\ m^{-2}\ hr^{-1} = \left[\frac{(C1-C2)}{T1} - \frac{(C1-C3)}{T2}\right] \times \frac{Vol}{Area},$$

where C1, C2 and C3 are as noted above, T1 and T2 are the incubation times (normalized to hours) of the cores and controls respectively, Vol is the water volume contained in the core, and Area is the substrate surface area within the core. Oxygen consumption values are reported for atmospheric pressure and test temperature during the experiments.

4.3.4 Redox Potential

The redox probe was made in the laboratory with platinum wire according to Hargrave (1972). Approximately 6 mm of 16 gauge platinum wire was soldered to about 90 cm of silver wire. The wire was run through a 1 mL disposable pipette with the platinum extending from the tip of the pipette. A Silicone sealant plug sealed the wire in at the tip of the pipette. The pipette was embedded through the plunger of a 50 ml disposable pipette. For precise measurements of probe penetration depths into the sediment as profiles were determined, the barrel of the syringe was clamped over the aquarium and the plunger moved up and down with a millimeter scale next to it. A Fisher Calomel Electrode (saturated KCL porous plug type, model 13-639-51) was used as a reference. Readings were made with the millivolt scale of a Corning Model 4 pH meter.

Before each use, the platinum electrode was cleaned with Ajax cleanser and then rinsed with distilled water. The two electrodes were placed in a beaker of saturated quinhydrone solution and the meter reading set to +275 mV. The electrodes were then rinsed and placed in the seawater overlying the substrate in the appropriate tank until the meter drift was ≤1 mV min^{-1}. The tip of the electrode was then lowered approximately 3 mm (all of exposed platinum)into the sediment using the clamped syringe. Millivolt readings were taken at the surface and at one cm intervals through the depth of the substrate. The potential of the calomel electrode against a standard hydrogen electrode (-241.5 mv) was added to measured potentials to calculate Eh [e.g. Eh = reading + (-241.5)]. The electrode was brought back up into the seawater for a final seawater reading and then cleaned.

4.3.5 Metals in Pore Water

Pore water metal concentration changes with time were measured to determine potential metal mobilization from sediments as redox conditions changed under the cuttings layers. This evaluation was performed on the 15 and 1 mm cuttings layers over fine sediment. Pore water samples were taken on days 1, 15, and 30. Eighteen inverted capped core tubes were prepared for each treatment. Three cm of fine sediment was placed in the tube and covered with the appropriate thickness of cuttings slurry. The tube lengths were just sufficient to hold the sediments and cuttings. The filled, inverted cores were then placed on the bottom of an empty aquarium with seawater flowing through. On each sampling day, 6 replicate cores were removed and grouped to make 3 replicates of 2 cores each. The pore water was squeezed from the cores under a nitrogen atmosphere. All of the following procedures were performed in the nitrogen atmosphere of a glove bag. The surface water was decanted off the cores and the two cores forming a replicate were emptied into a polypropylene filter holder containing a Seastar nitric acid rinsed Nucleopore polycarbonate filter (0.4 um, 142 mm diameter). High purity nitrogen was passed into the filter assembly and the pore water (approximately 25 mL) collected in acid rinsed teflon screw cap sample vials. Between replicate samples, the filter holder was cleaned with dilute nitric acid and Super-Q water. Samples were acidified to pH 1.5 with Seastar HNO_3.

The trace metals were extracted from the sample using XE-305 8-hydroxyquinoline (XE-305 8HQ) columns. One millilitre of the sample was diluted to ca. 250 mL with MQ water. The pH of the solution was adjusted with Seastar NH_4OH to pH 8. The pH of the solution was stabilized by adding 5 mL of pH 8 buffer (NH_4CL - NH_4OH), and the sample was passed through an XE-305 8HQ (10 mL bed volume) column. The flow rate through the column was kept at ca. 3 mL min^{-1}. Following the extraction, the column was washed three times with 30 mL of 1M HCl/0.1 M HNO_3 solution. Since high levels of Fe, Al and other metals preferentially chelated by 8-HQ were present in the samples, the capacity of the column could have been exceeded. Therefore, the first extraction elute was extracted a second time under identical conditions.

After appropriate dilution, the acid elutes were analysed for Zn, Cu, Pb and Cd content, using a Perkin-Elmer Model 703 atomic absorption spectrometer coupled to a HGA-500 graphite furnace.

For mercury analyses, subsamples of pore water (range 3.99 to 8.86 g) were weighed on a top loading balance and stored in acid cleaned Nalgene bottles. Samples were emptied into 500 mL Pyrex bottles and the Nalgene bottles were rinsed with 7 mL of H_2SO_4/HNO_3 (30%/80%) Baker TM grade and then 5 mL of cold tap water. The rinse solutions of acid and water were added to the pore water samples and heated at 85°C for 2 hours in a water bath. The stopcocks were inserted in the mercury bottles. Samples were taken out of the water bath and allowed to cool down overnight to room temperature. Cold tap water was added to make samples up to approximately 250 mL. Three millilitres of $SnCl_2/N_2SO_4$ (20%/80%) were added to the samples and Hg vapour was driven off with K grade nitrogen gas at approximately 7 to 8 psi into a 30 cm path length quartz cell of a Laboratory Data Controls U.V. monitor.

4.3.6 Metals in Sediment

Samples of the fine sediment and of the oiled cuttings were taken for analysis of Cd, Cu, Hg, Pb, Zn, Cr, Ni and V. Each sample was homogenized

by stirring, then subsamples withdrawn (approx. 10 g) and air dried to constant weight (approx. 24 hours). Sediments were then ground to a fine powder in an agate mortar.

Dried, ground samples were subjected to a $HNO_3/HClO_4$ hot acid leach as follows: Sediment samples (0.5 g) were heated in 28 cm (50 mL) tubes in a temperature controlled hot block with 5 mL HNO_3 for 30 minutes at 100°C. Five mL of $HClO_4$ were added to the cooled samples which were then heated for 15 minutes at 100°C. The tubes were cooled and washed down with 1 N HCl, then diluted to 50.0 mL in the tube with deionized water.

Total values for some metals (Cr, V, Zn) were obtained by a lithium metaborate fusion at 1100°C. Sample (0.1 g) melts were dissolved in 200 mL of 1.5% HCl solution.

The digests or acid leaches were analyzed by ICP (Quanta Trace Labs).

Hg was determined by heating 0.5 g dried samples along with 7 mL of HNO_3/H_2SO_4 (4:1) in 500 mL Pyrex glass bottles at 85°C for 2 hours. Samples were then cooled and diluted to 400 mL with tap water. The digest was split and the 200 mL aliquots analyzed as for pore water.

Recoveries were within the 95% tolerance limits of the certified values for reference materials.

4.4 Statistical Analyses

The standard error or the mean (S.E.M.) was calculated according to the formula:

$$\sigma = \frac{s}{n}$$

where s = the sample standard deviation. It was used as a measure of variability of the data and was often expressed as a percentage.

The Students t-test for comparison of means was used to test the hypothesis that the oxygen demand of various volumes of cuttings in the trial were equal to that of the control treatment where there were no cuttings.

A three-way analysis of variance using the classic experimental design approach with unequal cell frequencies was used for sedimentary oxygen demand rates versus cuttings depth, sediment type and time. The subprogram ANOVA of the SPSS statistical package was used (Nie et al., 1975). The dependent variable was oxygen consumption rate and the independent variables: sediment type, cuttings thickness and time were treated as non-metric variables for purposes of the ANOVA.

The quantitative relationship between oxygen consumption rates and the independent variables of time and cuttings layer thickness (treated as metric variables) were examined with the stepwise multiple regression procedure contained in the SPSS package of computer programs (Nie et al., 1975). After visual examination of the relationship between oxygen consumption rate and cuttings layer thickness, a logarithimic (base 10) transformation was applied to the thickness values. A constant of 0.05 was added to all values prior to transformation to permit the inclusion of the controls (0 mm) in the regressions.

Separate linear regressions were also run with the same statistical package to describe the relationship between oxygen demand and layer thickness at each of 15 and 30 days for the coarse and fine underlying sediments.

5.0 RESULTS

5.1 Test Material

The non-polar hydrocarbon content of cuttings stored for one year and used in these tests was not qualitatively different from the fresh cuttings (Figure 2). The stored sample had 22% lower total hydrocarbons than the fresh cuttings. This loss was accounted for by the resolved components of the non-polar hydrocarbons.

Control sediments consisted of a coarse grained sand collected from Lawrencetown Beach, Nova Scotia and a finer grained intertidal saltmarsh sediment from the same region. The first was 0% gravel, 99% sand, <1% silt and <1% clay. The second was <1% gravel, 83% sand, 15% silt and <1% clay. The particle size range of the cuttings was: 0% gravel, 48% sand, 50% silt and 2% clay. The total organic carbon contents of the coarse and fine sediments were 0.098% and 0.24% respectively, and that of the oiled cuttings was 3.13%.

5.2 Oxygen Measurement Method

When used in a closed flask with oiled cuttings, a polarographic oxygen probe gave erroneous readings after 5 days. Drift downward was substantial after 8 days (Table 2). This drift was attributed to fouling of the membrane with oil released from the cuttings. A dark, oily film was evident on the probe membrane at the end of the experiment. Based on the results of this trial, the micro-Winkler titration was used as the basic method of oxygen measurement for the remainder of the experiments.

5.3 Evaluation of Oxygen Change Detection Capabilities

The analytical method chosen for measuring changes in dissolved oxygen concentrations was sufficiently sensitive to detect these changes due to the volumes of cuttings that would be enclosed in core tubes during incubations

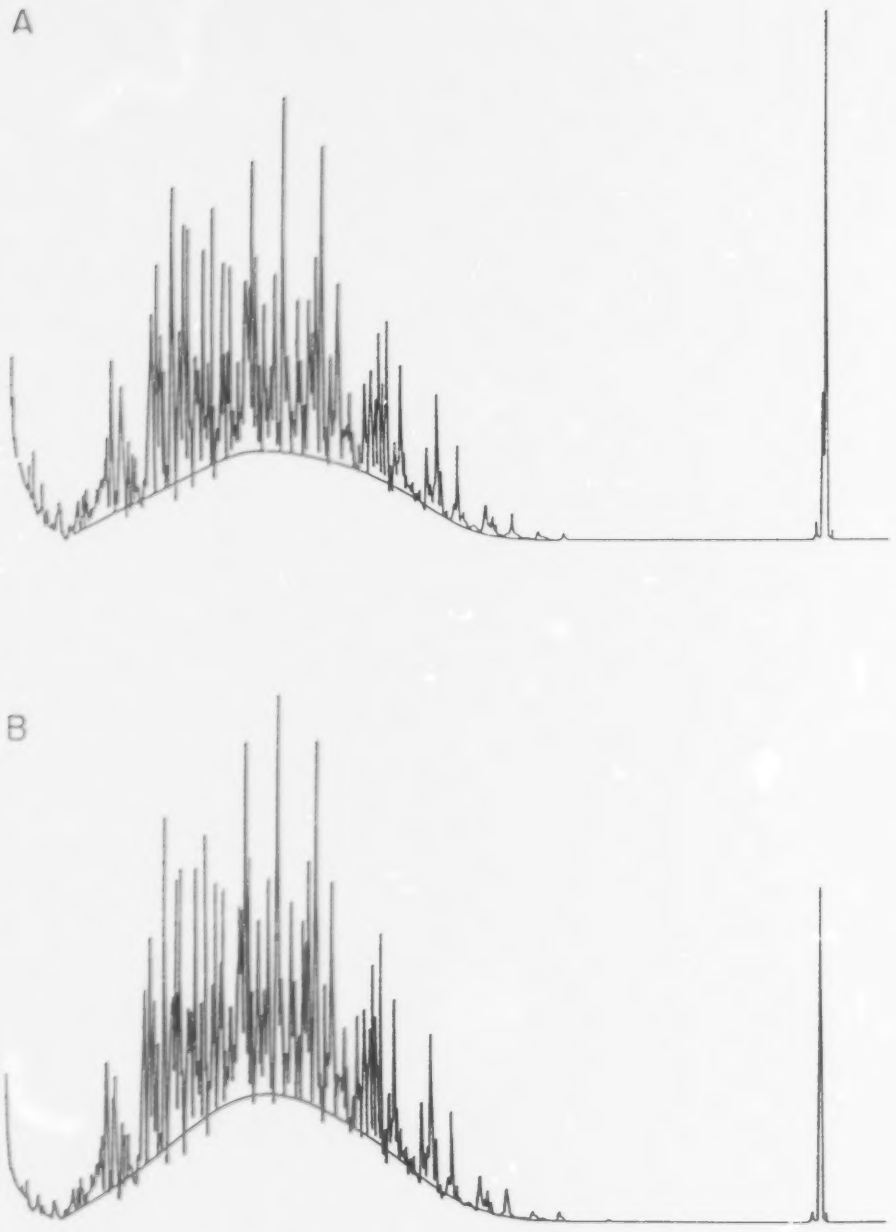

Figure 2. Gas chromatogram of non-polar hydrocarbons in Shell Alma F-67 cuttings.
A. Reanalysis of stored solvent extract from May 1984.
B. Cuttings stored 1 year at 4°C.

TABLE 2

COMPARISON OF WINKLER TITRATION AND POLAROGRAPHIC OXYGEN PROBE FOR MEASURING OXYGEN CONCENTRATION (mL O_2 L^{-1}) IN PRESENCE OF OILED CUTTINGS. VALUES ARE FOR INDIVIDUAL REPLICATES. MEANS ± 1 STD. ERROR SHOWN.

METHOD	TREATMENT	TIME (DAY) 0	2	5	8
Titrn	Control	9.95±0.06 (n=3)	9.43	9.58	11.05 11.32 11.19 11.19±0.08
Titrn	Sediment Control	-	9.87	5.68	5.43
Titrn	Cuttings	-	8.90	7.33 8.02 4.06 7.02 6.61±0.87	6.14 5.39 6.20 4.78 5.63±0.34
Probe	Cuttings	Set to 9.95	8.48	4.86	0.18

(Table 3). Each volume of cuttings representing the different cuttings thickness layers consumed oxygen at a rate that was significantly different from control water. The results of this trial indicated that oxygen demand of oiled cuttings was measurable with the micro-Winkler titration.

5.4 Oxygen Demand of Layered Cuttings

Raw data for the oxygen consumption rates of cuttings layered over natural sediments are contained in Appendix C. The data are presented in summary form in Figure 3. Values shown are the means and standard errors of three replicate cores per measurement. The value for each core was the mean of usually three replicate titrations. Variation between replicate titrations and amongst oxygen replicate dissolved determinations for each core was usually low with standard errors of generally <10.0% of the mean (Appendix C). Mean oxygen consumption rates for controls ranged between 0 and 6.5 mL O_2 m^{-2} hr^{-1} (Figure 3). All experimental values were within the range of 0 to 19.23 mL O_2 m^{-2} hr^{-1}. Differences amongst treatments were not large on days 1, 3 and 7 except for the coarse sediment control rates which had consistently lower oxygen consumption than the fine control or other treatments. As the experiment progressed, the oxygen demands of cuttings layered over sediments increased with respect to the appropriate controls. Distinctive differences between experimental treatments on the same days were most prevalent after 30 days.

The cuttings treatments layered over the fine sediments usually had higher oxygen consumption rates than those over coarse sediments. This was expected because of the higher natural organic content of the underlying sediments.

The magnitude of augmentation in oxygen demand rates for all experimental treatments relative to controls is shown in Table 4. The very large increases in the coarse sediment treatment on the first day were mainly a result of very low oxygen demand in the control. Thereafter, rates had increased by almost an order of magnitude over control values on day 15 and by an average of about 2 on day 30.

TABLE 3

TRIAL OF OXYGEN DEMAND OF VARIOUS VOLUMES OF CUTTINGS IN SMALL CONTAINERS (T = 24 hr)

PLANNED LAYER THICKNESS (mm)	CUTTINGS VOLUME (cm^3)	OXYGEN CONCENTRATION CHANGE (mL O_2 L^{-1})	$\bar{x} \pm 1$ STD. ERROR
15	54	-1.531 -1.180 -0.936	-1.22 ± 0.17*
2.5	9	-0.872 -0.791	-0.83 ± 0.04*
1.0	4	-0.223 -0.376 -0.236	-0.28 ± 0.05*
0	0	+0.472 +0.365	+0.42 ± 0.05

* Significantly different from control at $\alpha = 0.05$ (t-test)

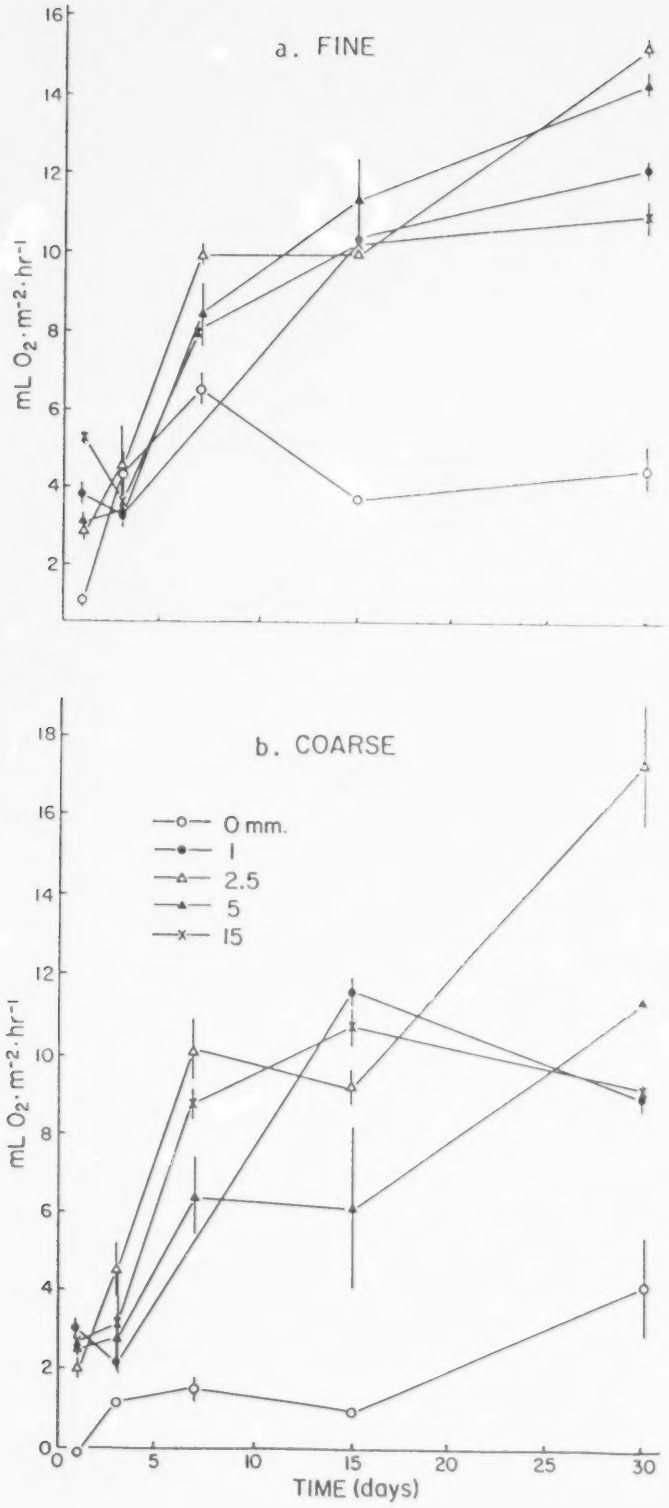

Figure 3. Sediment oxygen demand for oiled cuttings layers over sediments. a. fine sediments, b. coarse sediments.

TABLE 4

AUGMENTATION IN OXYGEN DEMAND RATE RELATIVE TO CONTROLS FOR OILED CUTTINGS LAYERS [(EXPTL - CONTROL)/CONTROL]

UNDERLYING SEDIMENT	CUTTINGS THICKNESS (mm)	DAY 1	3	7	15	30
Coarse	1	22.5	0.9	-	11.5	1.2
	2.5	14.4	2.9	5.9	8.9	3.2
	5	18.3	1.4	3.3	5.5	1.7
	15	18.7	1.8	4.9	10.5	1.2
	Mean	18.5	1.8	4.7	9.1	1.8
Fine	1	2.7	-0.2	-	1.8	1.7
	2.5	1.7	0.1	0.5	1.9	2.4
	5	2.0	-0.3	0.3	2.0	2.2
	15	4.0	-0.2	0.2	1.8	1.4
	Mean	2.6	-0.2	0.4	1.9	1.9

Results of the ANOVA (Table 5) indicated that there was a highly significant sediment type x cuttings depth interaction as well as a cuttings depth x day interaction, but no sediment type x day interaction. Not surprisingly, the main effects of the variables were significant. The curves in Figures 3 a and b illustrate the interaction between cuttings depth and day. Cuttings layers seem to have a greater effect on sedimentary oxygen demand after longer periods of time.

A significant three-way interaction between all independent variables indicated that the interaction between any pair of the three variables depended on the level of the third variable.

The oxygen consumption rate, O_2 (expressed as negative values in units of mL O_2 m^{-2} hr^{-1}), of the cuttings at approximately 1°C can be predicted by a multiple regression equation with the time (days) and cuttings thickness (mm) as independent variables.

FINE UNDERLYING SEDIMENT:

$$O_2 = -3.68 - 0.27\ TIME - 1.60\ LOG_{10}\ (THICKNESS + 0.05)$$

COARSE UNDERLYING SEDIMENT:

$$O_2 = -2.25 - 0.28\ TIME - 2.26\ LOG_{10}\ (THICKNESS + 0.05)$$

The equations account for 66.5 and 59.4% respectively of the variation in observed oxygen consumption rates (multiple r's = 0.81 and 0.77) and are signficant at $\alpha \leq 0.01$.

The relationship between oxygen consumption rate and the cuttings layer thickness is illustrated in Figure 4 for the 15 and 30 day exposures over coarse and fine sediments. Oxygen consumption rates after 15 and 30 days were increased relative to controls by the deposition of cuttings layers up to about 2 mm in thickness. Thicker cuttings layers resulted in lower rates after 30 days than the thinner layers, however the rates were still greater than controls.

TABLE 5

ANALYSIS OF VARIANCE TABLE FOR SEDIMENT OXYGEN DEMAND (ML O_2 M^{-2} HR^{-1}) VERSUS SEDIMENT TYPE, CUTTINGS DEPTH AND DAY

Source of Variance	Sum of Squares	DF	Mean Square	F	Significance of F
Main Effects	4,873.576	9	541.508	499.374	0.001
Sediment Type	154.396	1	154.396	142.382	0.001
Cuttings Depth	1,530.644	4	382.661	352.886	0.001
Day	3,448.272	4	862.068	794.991	0.001
2-Way Interactions	890.797	23	38.730	35.717	0.001
Sediment Type, Cuttings Depth	64.232	4	16.058	14.809	0.001
Sediment Type, Day	0.299	4	0.075	0.069	0.991
Cuttings Depth, Day	821.183	15	54.746	50.486	0.001
3-Way Interactions	171.384	15	11.426	10.537	0.001
Sediment Type, Cuttings Depth, Day	171.384	15	11.426	10.537	0.001
Explained	5,935.757	47	126.293	116.466	0.001
Residual	329.650	304	1.084		
Total	6,265.407	351	17.850		

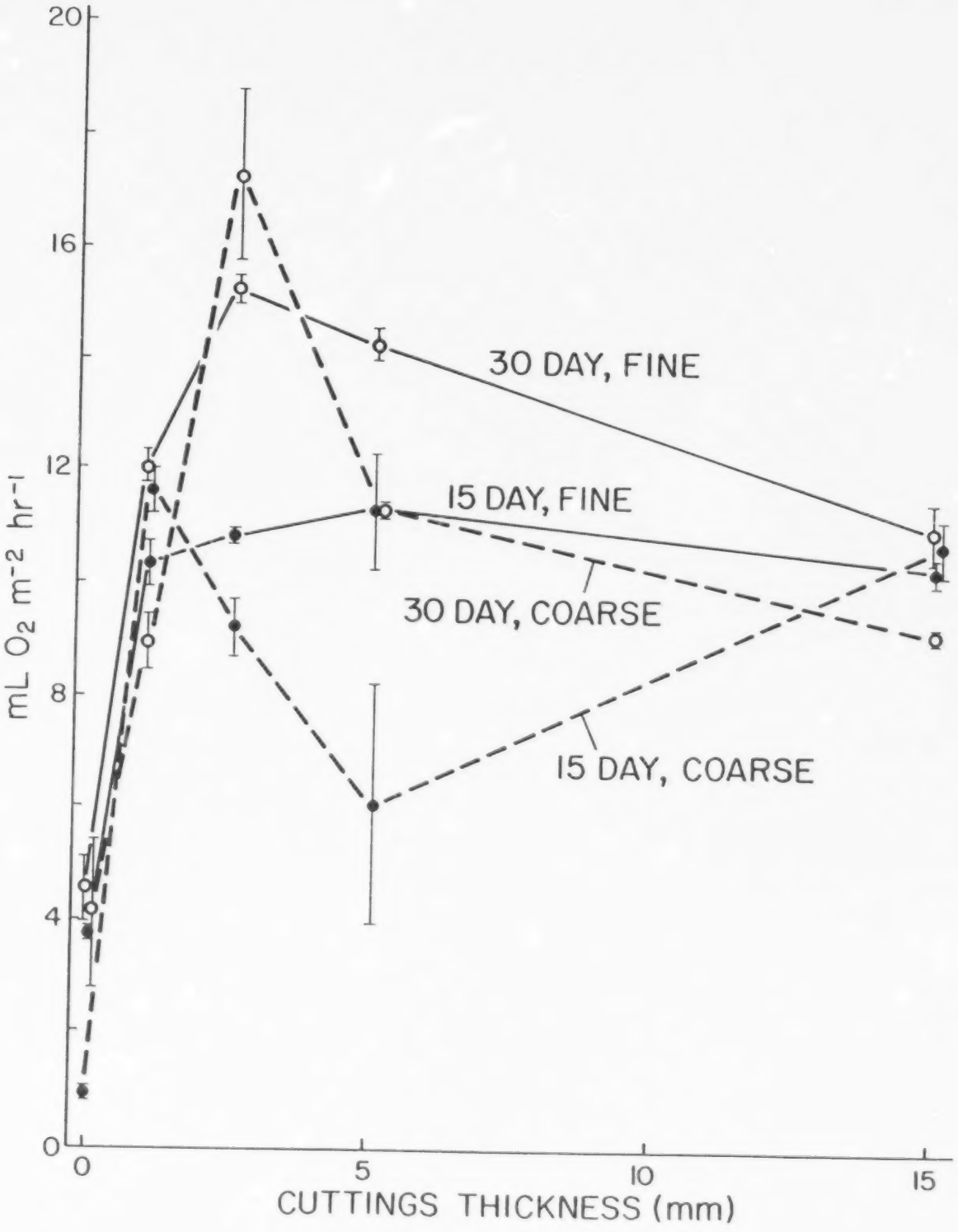

Figure 4. Sedimentary oxygen demand versus oily cuttings layer thickness after 15 and 30 days over coarse and fine natural substrate. Means ± 1 standard error shown.

TABLE 6

SEDIMENTARY OXYGEN DEMAND (mL O_2 m^{-2} hr^{-1}) AS A FUNCTION OF CUTTINGS LAYER THICKNESS. CURVE PARAMETERS FOR CURVE OF FORM: $O_2 = a + b \log_{10}$ (thickness + 0.05).

DURATION (d)	UNDERLYING SEDIMENT TYPE	EQUATION COEFFICIENTS a	b	r	signficance
5	Coarse	-7.04	-3.36	0.68	.01
	Fine	-8.68	-2.94	0.87	.01
30	Coarse	-9.65	-2.92	0.55	.05
	Fine	-10.74	-3.39	0.75	.01

For a fine or coarse underlying sediment, the oxygen demand rate of cuttings layered over the sediment can be predicted by the equations shown in Table 6.

5.5 Redox Potential Variation

Redox potentials in the sediments versus depth are plotted in Figure 5 for observations on days 1, 3, 7, 15 and 30 of the experiments. Redox values ranged from -173 to +118 mV. Eh valves did not exhibit consistent patterns of change with depth or time. Decreases in redox potential occurred most frequently in the fine sediment treatment and usually on day 3 of the 30 day experiment. There were increased gradients between the surface and underlying sediments on days 7 and 15 as well in the 5 mm cuttings layer treatment.

In coarse sediment treatments, strong Eh gradients were not observed even under layers of cuttings up to 15 mm thick.

5.6 Metals

Metal concentrations in the oiled cuttings and fine sediment are summarized in Table 7. The accuracy of the analyses reported here with respect to published values for standard reference material is also shown in Table 7. Agreement was generally good in all cases. The oiled cuttings had higher concentrations of all detectable metals than the natural fine sediments. The differences were more than an order of magnitude in some cases. This finding is not unexpected because of the presence of various metals in additives to drill fluids.

Metals concentrations in pore water samples are given in Table 8 for Hg, Cu, Cd, Pb and Zn. The samples proved to be very difficult to analyze for Cu, Cd, Pb and Zn because of the presence of oil in the samples. Hence, only fine ground samples under the 15 mm layer of cuttings were tested as it was assumed that this would represent a "worst case" situation.

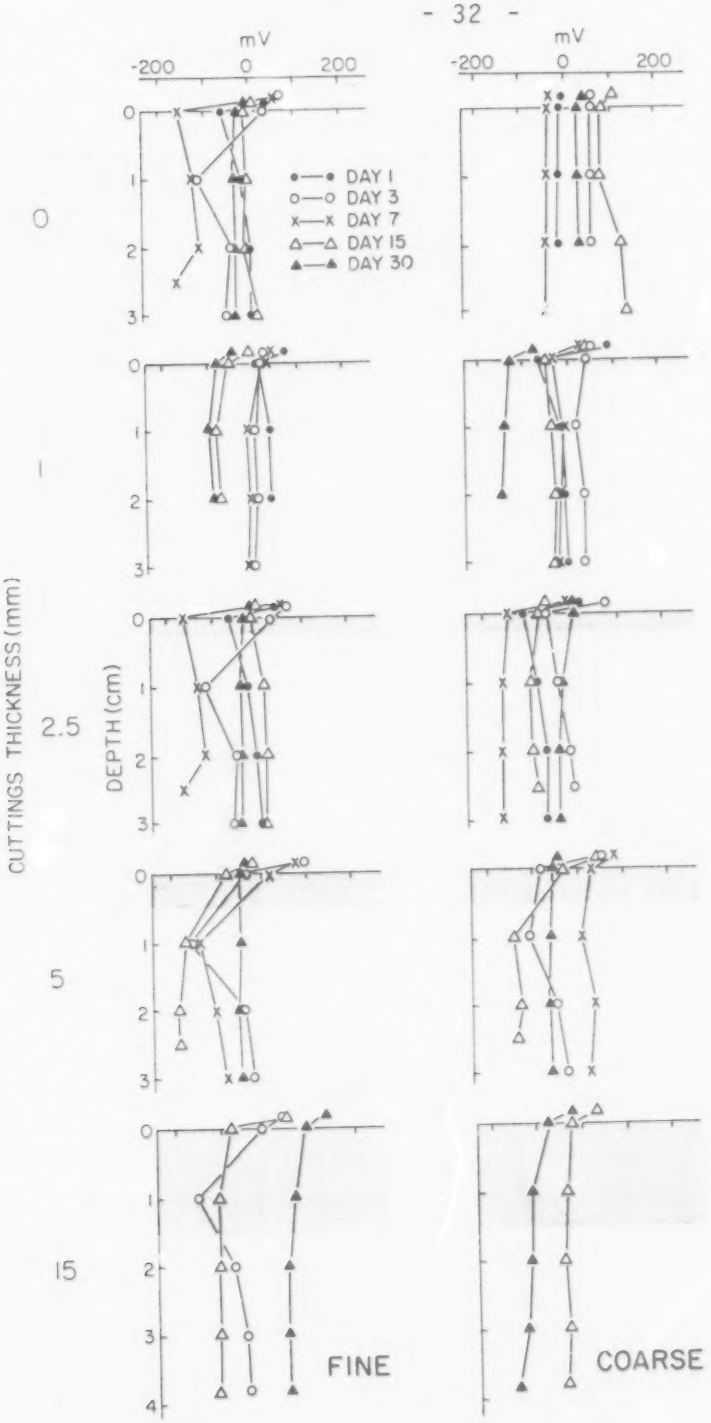

Figure 5. Redox potential under cuttings layers with time. Shadowed areas represent cuttings thicknesses.

TABLE 7

TRACE METALS IN SEDIMENT

	SAMPLE		NRC MESS-1	
ELEMENT	FINE SEDIMENT	OILED CUTTINGS	REFERENCE VALUE	FOUND
Cd	<0.5	<0.5	0.59	<0.5
[a]Cr	18 ± 14	123 ± 12	71	69
Cu	3 ± 0	47 ± 11	25.1	22
Hg	0.019 ± 0.01	0.118 ± 0.05	0.171	0.169
Ni	6 ± 0	77 ± 10	29.5	21
Pb	<5	698 ± 1	34.0	29
[a]V	43 ± 5	167 ± 6	72.4	75
[a]Zn	40 ± 0	233 ± 12	191	200

NOTE: Results in ug g^{-1}; given as mean ± standard deviation (n=3).
[a] lithium metaborate fusion

TABLE 8

METALS IN SEDIMENT PORE WATERS

DAY	CUTTINGS THICKNESS	METAL CONCENTRATION (ng g^{-1}) Hg	Cu	Cd	Pb	Zn
1	1 mm	92*				
		29*				
	15 mm	3.4	140	<0.7	23	491
		6.4	126	<0.7	23	468
15	1 mm	8.8				
		8.2				
	15 mm	7.3	443	<0.7	29	277
		4.8	435	<0.7	21	318
30	1 mm	3.6				
		12.2				
	15 mm	6.4	422	<0.7	19	167
		4.6	546	<0.7	21	190

* apparently contaminated in collection or analysis

Both Hg and Pb concentrations were unchanged in pore waters during the 30 day period. Cadmium levels were below detection in all instances. Copper and zinc showed opposite trends. Zinc concentration decreased steadily with time while Cu levels increased by a factor of 4 after 15 days and remained at that level after 30 days.

6.0 DISCUSSION

6.1 Oxygen Demand

The total sedimentary oxygen demand of subtidal marine sediments will be increased if oily drill cuttings are deposited on top of the sediments. This study was conducted under near arctic water temperatures (approximately 1°C) and easily measurable increases in sedimentary oxygen demand occurred as a result of layering cuttings over natural sediments. The magnitude of the increase was dependent upon the cuttings layer thickness, the time after application and the texture of the underlying sediments.

The cuttings used in this study were from the Shell F-67 well where a Conoco "low-toxicity" mineral type oil was used. The oil consisted primarily of branched alkanes and substituted cyclohexanes with less than 1% aromatics. The aromatics were primarily substituted. The residual oil content of the cuttings was 9.5% total non-polar hydrocarbons determined by gc-ms (Hutcheson et al., 1984). The cuttings were 48% sand, 50% silt and 2% clay with a total organic carbon content of 3.13%. This carbon content was substantially greater than either that of the coarse (0.098%) or fine (0.24%) natural marine sediments used in the experiments. Marine sediments with oil contents as high as those of the cuttings do not normally occur, however oily cuttings with total petroleum hydrocarbon concentrations as high as those measured here generally are limited to within distances of <200-500 m from discharge sites around drilling platforms where oil base muds are used (Davies et al., 1984).

There are no comparative data presently available on the oxygen demands of oily cuttings on the seafloor although other studies in progress or not yet published have also addressed this topic in field or microcosm experiments using diesel and early generation mineral type oils (Section 3.0).

The oxygen demand of subtidal marine sediments at depths less than about 200 m ranges from 2.9 to 120 mL O_2 m^{-2} hr^{-1} on a world-wide basis (Table 9). Zeitzschel (1981) noted that the average value for these waters

TABLE 9. TOTAL OXYGEN DEMAND OF MARINE SEDIMENTS. SUMMARIZED FROM LITERATURE.

Rate ($mgO_2\ m^{-2}\ h^{-1}$)*	Location	T (°C)	Depth (m)	Core/In Situ (C/I.S.)	Reference
3.7-100.4 (av=26.1)	-	-	0-200	-	Zeitzschel, '81
14.8 - 59.8	Buzzards Bay	1.5-16	17	I.S.	Rowe et al., '75
77.97	Buzzards Bay	July, Aug	15	I.S.	Smith et al., '73
34.6 - 37.8	Buzzards Bay	18-20	12-14	C	Florek & Rowe, '83
9.6-4.96	Kiel Bight	9.5-13.9	20	I.S.	Balzer et al., '83
13.87	Kiel Bight	8-13	20	I.S.	Balzer, '84
5.54	Kiel Bight	4.9	20	I.S.	Balzer, '84
9.58	Kiel Bight	9.5	20	I.S.	Balzer et al., '83
5.7-49.98	Bedford Basin	2-4.5	60	C	Hargrave, '78
5.71-71.4 (av=29.3)	Eastern Passage	0.7-16	0.5-2	I.S.	Hargrave & Phillips, '81
6.56	Randers Fjord	3		C	Revsbech et al., '80
11.68	Estuary	10		C	Revsbech et al., '80
44.8	Estuary	18		C	Revsbech et al., '80
8-48	Limfjorden, Denmark	3-19	4-12	C	Jørgensen, '77
21.4	Eckernforde Bight (S.W. Baltic)	13.2	11	I.S.	Pamatmat et al., '81
20.8-85	Chesapeake Bay	0-27	3	I.S.	Kemp & Boynton, '81
10-141	Chesapeake Bay	0-27	6	I.S.	
20.8-170.8	Patuxent Estuary	3-29	3	I.S.	Boynton et al., '80
10-150 (av=4.1)	Narragansett Bay	0-24	5.8-7.3	I.S.	Nixon et al., '76a
4.7-107.3 (av=37.8)	Narragansett Bay	3.2-22.4	5.8-7.3	I.S.	Hale, '76
20.8	Gay - Head Burmuda	2	40	I.S.	Smith, '78
43.4	Transect	13	40	I.S.	Smith, '78
40.8	Transect	14	40	I.S.	Smith, '78
0.7-4.8 av=1.4	Spanish Continental Shelf	20	94-238	C	Tenore et al., '84
28.4	Castle Harbor, Bermuda	19	1.5	I.S.	Smith et al., '72
36.8	Castle Harbor, Bermuda	23	1.5	I.S.	Smith et al., '72
55.8	Baja, California	13	23	I.S.	Smith et al., '74

Table 9 (continued)

Rate ($mgO_2\ m^{-2}\ h^{-1}$)*	Location	T (°C)	Depth (m)	Core/In Situ (C/I.S.)	Reference
40.4	Baja, California	13	29	I.S.	Smith et al., '74
30.6	Spanish Sahara	16	30	I.S.	Smith et al., '76
6.2	E Trop. Pacific	15	85	C	Pamatmat, '71
5.4	E Trop, Pacific	15	275	C	(in Hargrave, '73)
44.1	La Jolla, Cal.	15	17	I.S.	Smith et al., '78
76.97-132.4	Sapelo Is, Georgia	6.8-28.5	7	C	Smith, '73
121	Georgia Bight	28	3.8	I.S.	Hopkinson & Wetzel, '82
1.86	Christiaensen Basin (N.Y. Bight)	7.8	35.5	I.S.	Rowe et al., '77
2.86-47.1	N.Y Bight	11-23	13-28	I.S.	Florek & Rowe, '83
8.14-47.6	E.N.Y. Bight	10-16	20-150	C	Florek & Rowe, '83
5.43-10.6	Georges Bank	6-14	55-155	C	Florek & Rowe, '83
8.7-17.24	Carmarthen Bay, UK	7.6-17.1	9.8-17.3	C	Pomeroy et al., '83
29.1	Long Is. Sound	10	20	C	Carey, '67
9.6	Puget Sound	9	180	C	Pamatmat, '71a
11.0	Puget Sound	7	23	C	Pamatmat, '71a
11.0	Puget Sound	7	22	C	Pamatmat, '71a
12.8	Puget Sound	7	22	I.S.	Pamatmat, '71a
5.7-57.1	Puget Sound	7-15	11-180	I.S.	Pamatmat & Banse, '69
27.1	Puget Sound	12.2	30	I.S.	Pamatmat & Banse, '69
50	Puget Sound	15.2	15-18	I.S.	Pamatmat & Banse, '69
50	Puget Sound	13.5	75-80	I.S.	Pamatmat & Banse, '69
47.1	Puget Sound	12.3	20-23	I.S.	Pamatmat & Banse, '69
24.2	Puget Sound	11.3	180	I.S.	Pamatmat & Banse, '69
35.7	Puget Sound	11.9	70	I.S.	Pamatmat & Banse, '69
9.6	N.E. Pacific	7	146	C	Pamatmat, '71b
4.2	N.E. Pacific	7	105	C	Pamatmat, '71b
4.86	N.E. Pacific	7	146	C	Pamatmat, '71b
8.7	Camarthen Bay	7.6	10	C	Pomeroy et al., '83
17.24	Camarthen Bay	14.8	10	C	Pomeroy et al., '83
14.17	LaJolla Bight	-	18.3	I.S.	Hartwig, '76

* 1.43 mg O_2 = 1 mL O_2

was 37.3 ml O_2 m^{-2} hr^{-1}. None of the data were for polar marine waters. The temperature dependence of these rates is illustrated in Figure 6 and suggests that natural arctic marine sediments at depths less than 200 m should have total sedimentary oxygen demands of less than about 8 ml O_2 m^{-2} hr^{-1}. This range would encompass water temperatures less than about 5°C.

Control oxygen consumption rates measured during this study were in this range of from about 0-6 ml O_2 m^{-2} hr^{-1} and are in line with those expected at these temperatures. Rates in the experiments may be artificially low because of the deliberate defaunation of the natural sediments by drying prior to use. Oiled cuttings deposited over the natural sediments increased the background oxygen demand of the sediments by 0.2 to 18.5 times. Maximum oxygen consumption rates were about 9 times those of controls after 15 days (Table 4).

The oxygen demands of fine control sediments and cuttings deposited over these sediments were generally greater than those of the coarse control sediments or experimental treatments. This result is expected because of the higher organic content of the finer sediments which serves as a substrate for oxidative metabolic processes by bacteria.

Once cuttings were applied to natural sediments, differences between experimental treatments and controls appeared within 1 to 7 days (Figure 3). Differences amongst treatments do not become apparent until 2 to 4 weeks after the start of the experiment. This time delay may be due in part to the time required for oleophilic microbial populations to establish themselves on the cuttings and for natural heterotrophs to recolonize the underlying sediments.

Cuttings layer thicknesses between 1 and 15 mm were used in this experiment. The experimental results and those of other workers (Section 3.0) suggest that there may be a threshold effect of oiled cuttings on oxygen demand characteristics of subtidal substrates. Thin layers of cuttings (<2 mm) may incompletely cover underlying sediments or be thin enough to permit gaseous and elemental exchange processes between underlying sediments

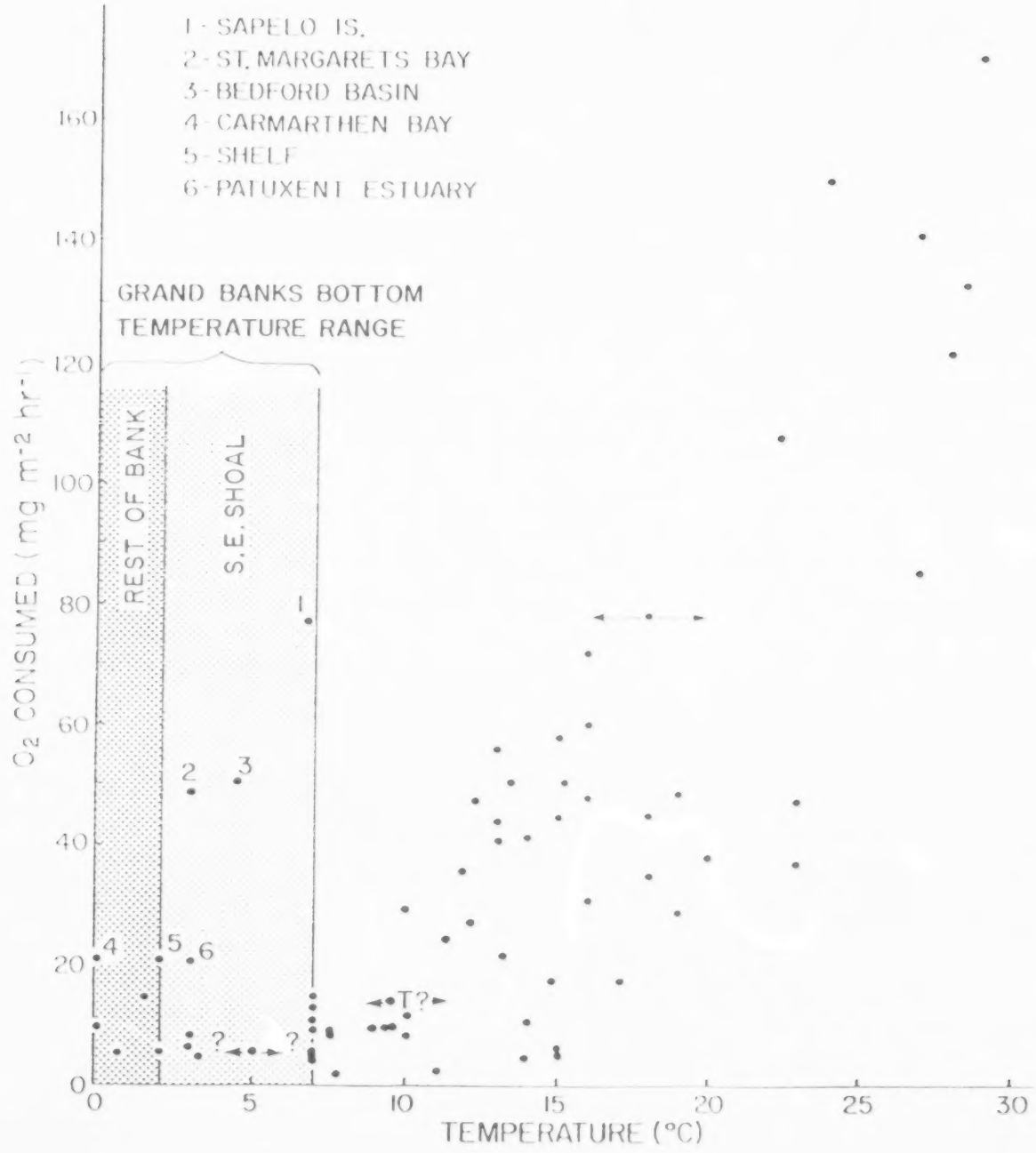

Figure 6. Total benthic community oxygen demand versus temperature. Summarized from literature. (1 mg O_2 L^{-1} = 1.43 mL L^{-1})

and overlying waters. In these instances, the oil may serve as an organic metabolic substrate for bacteria which is additional to the natural organic carbon pool of the underlying sediments. The combination of these two sources of carbon is reflected in a high metabolic oxygen demand after 30 days (Figure 4). Cuttings layers thicker than approximately 2 mm progressively inhibit exchange processes between underlying sediments and overlying waters. Oxygen demand measurements are therefore primarily measuring the oxygen demand associated with metabolic activity on or near the cuttings surface. Although the experiments described in this report did not test layers thicker than 15 mm, the oxygen demand of layers thicker than this should be the same after several weeks as that for the 15 mm case, since cuttings layer thicknesses greater than a threshold would presumably have the same effects on exchange processes with the underlying sediments.

When the gaseous exchange route up through surficial sedimentary material is cut off or restricted, natural metabolic processes within sediments will continue aerobically until available oxygen is consumed or switch to anaerobiosis where possible. These alterations in metabolic activities are usually reflected in physico-chemical charges in the sediments; most notably the redox chemistry as indicated by Eh, the redox potential. After the application of various thicknesses of cuttings layers over natural marine sediment, moderate changes in the redox chemistry of the sediments were observed over 30 days. Vertical Eh gradients were generally not observed through cuttings into coarser sediments. Decreases in the Eh of underlying sediments were recorded in fine sediment treatments with cuttings layers of thicker than 2.5 mm (Figure 5). Field monitoring around an oiled cuttings discharge site has defined a core of greatly reduced Eh (approximately -200 mV) within 100 to 200 m of the discharge and a return to normal Eh values of >200 mV beyond that (Addy et al., 1984). The minimum Eh values measured in this study (-173 mV) approached these values. These results from the field are indicative of the smothering effect that oiled cuttings can have on underlying sediments. In the experiments described in this report, the low temperature and associated low rates of metabolic activity may have reduced the rate at which sediment redox potential changed over 30 days relative to field conditions in the North Sea. For comparison, a theoretical calculation of the time to exhaustion of the dissolved oxygen

supply can be made:

1. Initial pore water dissolved oxygen concentration, est. $\underline{10\ mL\ O_2\ L^{-1}}$ (same as overlying water)
2. Fine sediment oxygen demand rate: $\underline{5\ mL\ O_2\ m^{-2}\ hr^{-1}}$
3. Oxygen content of 1 m^2 sediment x 5 cm deep:

   100 cm x 100 cm x 5 cm = 50,000 cm^3 sediment

   Assume 30% water content

   = $\underline{15,000\ cm^3\ pore\ water}$

   x 10 mL O_2/1000 cm^3

   = $\underline{150\ mL\ O_2}$
4. Time to consume all available oxygen:

   150 mL $O_2\ m^{-2}$ / 5 mL $O_2\ m^{-2}\ hr^{-1}$

   = $\underline{30\ hr}$
5. Assumptions
   - no gaseous exchange with overlying water
   - oxygen consumption rate of sediments constant, not regulated.

It appears that complete exhaustion of the oxygen supply in fine sediments should occur within days if the sediments are covered by oiled cuttings layers that prevent gaseous exchange. The experimental results suggest that the rate of change in redox chemistry is much slower. One factor which could have influenced our results is the opportunity for water exchange each time core tubes were driven into the sediments and removed. A route for water exchange was provided by the hole left in the sediments from the tube.

6.2 Release of Trace Metals

The experiments also examined the potential release of metals into pore waters as the experiment progressed. The results suggest that mobilization of Hg, Pb, Cd and Zn from oiled cuttings should not occur under conditions similar to those in this experiment. The 15 mm cuttings layer over fine sediments represents a worst case condition in terms of the potential for changes in sediment redox chemistry. Increases in Cu pore water concentrations

did occur. The magnitude of an increase will probably alter under varying Eh conditions, as well as sediment types and nature and concentration of organic material. This trend may be reversed as sediment Eh decreases. Most metals form insoluble sulfide complexes if H_2S is present.

The reasons for the observed difference in behaviour of copper and zinc in this study are unclear. Copper forms strong complexes with a variety of organic compounds and its increased pore water concentrations may be a result of increased solubility of organic complexes. It is also possible that changes in the Eh of the sediment may have been such as to induce the dissolution of copper bearing mineral phases or complexes while Zn was being sequestered or absorbed onto sediment particles.

7.0 SUMMARY

1. The micro-Winkler titration was the most appropriate method for oxygen content measurements with oiled cuttings because of oil fouling problems with the probe membrane over time.

2. Natural marine sediments had oxygen consumption rates of about 0 to 4 mL O_2 m^{-2} hr^{-1} (fine sediment) and 1 to 7 mL O_2 m^{-2} hr^{-1} (coarse sediments).

3. Oiled cuttings layered over the natural sediments resulted in an increase in sediment oxygen consumption rate up to 18 fold above controls. Rates for these treatments ranged from 0 to 19.23 mL O_2 m^{-2} hr^{-1}.

4. The oxygen demand of cuttings layered over natural sediments can be predicted by the following equations validated at about 1°C for cuttings thicknesses up to 15 mm over 30 days:

$$O_2 = -3.68 - 0.27\ day - 1.60\ \log_{10}(thickness + 0.05)$$
for fine sediment treatments

$$O_2 = -2.25 - 0.28\ day - 2.26\ \log_{10}(thickness + 0.05)$$
for coarse sediment treatments.

5. Fifteen to thirty days are required for differences between treatments to appear.

6. Maximum augmentation of oxygen demand occurs with a 2.5 mm thick cuttings layer. The rate of oxygen demand tends to drop slightly beyond that point.

7. The redox potential through the cuttings and underlying sediments decreased to minimum value of -173 mV over 30 days. Greatest changes occurred with the fine sediment treatments.

8. The magnitude of changes in the redox chemistry was similar to that recorded in other field studies.

9. Pore water concentrations of copper increased about 4 fold during the experiment under 15 mm of cuttings layered over fine sediments. Zinc concentrations decreased similarily. Mercury, cadmium and lead concentrations did not change.

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APPENDIX A
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APPENDIX A

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APPENDIX B

Oxygen Titration Method

APPENDIX B

MICRO WINKLER TITRATION METHOD

BLANK RUN - Before Each Series of Analyses

1. Pipette 1 ml potassium iodate into a 125 ml flask and add 50 ml distilled water.
2. Add 1/2 ml conc. sulfuric acid and 1/2 ml alkaline iodide.
3. Stir for 1 minute and add 1/2 ml manganous sulfate and 1 ml starch.
4. Place flask under delivery tip and titrate until solution is just colorless.
5. Record volume added (1).
6. Pipette 1 ml potassium iodate into this same solution and stir for 1 minute.
7. Titrate until just colorless and record volume added (2).
8. The difference between the 2 titrations (1-2) is the reagent blank (±0.0010 ml). It may be positive or negative.

STANDARDIZATION - Before Each Series of Analyses

1. Pipette 5 ml potassium iodate into a flask and add 50 ml distilled water.
2. Add 1/2 ml conc. sulfuric acid and 1/2 ml alkaline iodide and stir for 1 minute.
3. Titrate until pale yellow and add 1 ml starch. Continue titrating until solution is just colorless. Record volume.
4. Run 2 more standardizations (±0.0005 ml).

SAMPLE TITRATION

1. To each syringe add 1/2 ml manganous sulfate and 1/2 ml alkaline iodide, seal with parafilm and shake.
2. Let syringe stand until precipitate has settled a bit, then add 1/2 ml conc. sulfuric acid, seal again and shake until all precipitate has dissolved. Empty contents into flask.
3. Add stirring bar and titrate with sodium thiosulfate until pale yellow color.
4. Add 1 ml starch.
5. Continue titrating to end point (just colorless).
6. Record volume added.
7. Reset buret and do next sample.

NOTE: All samples should be acidified before starting the series of titrations.

APPENDIX C
Raw Data Tables

TABLE C-1. RAW DATA TABLES OF OXYGEN CONSUMPTION RATES (mL O_2 m^{-2} hr^{-1}) CALCULATED FROM INDIVIDUAL WATER SAMPLES TAKEN FROM REPLICATE CORES (MEANS ± 1 STD. ERROR OF MEAN SHOWN).

TREATMENT Cuttings(mm)	Sediment	REPLICATE CORE		SAMPLING DAY 1	3	7	15	30
0	Fine	A		0.92	6.43	7.01	3.94	5.04
				0.85	6.21	7.52		4.97
				1.35	-1.97			7.32
			$\bar{x}$	1.04±0.16	3.56±2.76	7.27±0.26	3.94±0.00	5.78±0.77
		B			5.81	6.54	3.82	4.16
					5.25	6.25	3.55	3.58
					5.25	6.75	3.62	4.16
							3.69	
			$\bar{x}$		5.44±0.19	6.51±0.15	3.67±0.06	3.97±0.19
		C			3.90	5.12	3.55	4.03
					3.96	6.28	3.45	3.48
					3.76	5.94	3.76	4.03
			$\bar{x}$		3.87±0.06	5.78±0.34	3.59±0.09	3.85±0.18
		Grand Mean		**1.04±0.16**	**4.29±0.58**	**6.52±0.43**	**3.73±0.11**	**4.53±0.62**
0	Coarse	A		-0.00	1.34	0.69	0.34	1.92
				-0.31	1.48	1.24	1.64	2.48
				-0.46	1.05	0.76	1.37	2.30
			$\bar{x}$	-0.26±0.14	1.29±0.13	0.90±0.17	1.12±0.40	2.23±0.17
		B		-0.22	1.09	1.84	0.53	3.14
				0.22	1.09	1.84	1.59	3.59
				0.14	1.57	1.37	0.53	3.71
			$\bar{x}$	0.19±0.03	1.25±0.16	1.68±0.16	0.88±0.35	3.48±0.17
		C			0.27	1.73	1.08	6.70
					1.08	1.73	0.94	6.57
					1.41	2.14	0.34	6.82
			$\bar{x}$		0.92±0.34	1.87±0.14	0.79±0.23	6.70±0.07
		Grand Mean		**-0.13±0.13**	**1.15±0.12**	**1.48±0.30**	**0.93±0.10**	**4.14±1.33**

TABLE C-2. RAW DATA TABLES OF OXYGEN CONSUMPTION RATES (mL O_2 m^{-2} hr^{-1}) CALCULATED FROM INDIVIDUAL WATER SAMPLES TAKEN FROM REPLICATE CORES (MEANS ± 1 STD. ERROR OF MEAN SHOWN).

TREATMENT		REPLICATE		SAMPLING DAY				
Cuttings(mm)	Sediment	CORE		1	3	7	15	30
1	Fine	A		3.83	3.66		10.86	11.04
				4.61	2.27		10.61	11.70
				4.22	2.92		10.61	12.06
			$\bar{x}$	4.22±0.23	2.95±0.40		10.69±0.08	11.60±0.30
		B		3.04	3.01		9.59	12.16
				3.49	3.31		9.83	12.16
				3.12			9.30	12.16
				3.34				
			$\bar{x}$	3.25±0.10	3.16±0.15		9.57±0.15	12.16±0.00
		C		4.12	3.90		10.74	12.86
				3.97	4.20		10.74	12.64
				3.76	3.68		10.92	12.21
			$\bar{x}$	3.95±0.10	3.93±0.15		10.80±0.06	12.57±0.19
		Grand Mean		**3.81±0.29**	**3.35±0.30**		**10.35±0.39**	**12.11±0.28**
1	Coarse	A		2.89	1.76		11.87	8.39
				1.88	1.97		11.80	8.33
				2.53	2.11		12.00	
			$\bar{x}$	2.43±0.30	1.95±0.10		11.89±0.06	8.36±0.03
		B		3.04	2.90		10.61	9.54
				3.18	2.07		10.61	9.54
				3.46			11.23	9.73
			$\bar{x}$	3.23±0.12	2.49±0.42		10.82±0.21	9.60±0.06
		C		3.84	1.92		12.36	
				3.06	1.85		12.18	
				3.58	2.28		12.12	
			$\bar{x}$	3.49±0.23	2.02±0.13		12.22±0.07	
		Grand Mean		**3.05±0.32**	**2.15±0.17**		**11.64±0.42**	**8.98±0.51**

TABLE C-3. RAW DATA TABLES OF OXYGEN CONSUMPTION RATES (mL O_2 m^{-2} hr^{-1}) CALCULATED FROM INDIVIDUAL WATER SAMPLES TAKEN FROM REPLICATE CORES (MEANS ± 1 STD. ERROR OF MEAN SHOWN).

TREATMENT		REPLICATE	SAMPLING DAY				
Cuttings(mm)	Sediment	CORE	1	3	7	15	30
2.5	Fine	A	3.14	3.46	10.05	10.63	14.72
			3.02	3.68		10.45	
			3.43	3.63		11.23	
		$\bar{x}$	3.20±0.12	3.59±0.07	10.05	10.77±0.24	14.72
		B	2.90	5.89	9.36	10.90	15.81
			2.72	5.33	9.42	10.96	15.32
			2.90	5.44	9.42	10.60	15.18
		$\bar{x}$	2.84±0.06	5.55±0.17	9.40±0.02	10.82±0.11	15.44±0.19
		C	2.60		10.25	11.04	15.28
			2.60			10.98	15.83
			2.32			10.98	
		$\bar{x}$	2.51±0.09		10.25	11.00±0.02	15.56±0.28
		Grand Mean	**2.85±0.20**	**4.57±0.98**	**9.90±0.26**	**10.86±0.07**	**15.24±0.26**
2.5	Coarse	A	1.68	5.72	10.19	9.69	14.31
			1.61	5.61	9.36	8.50	14.04
			1.55	6.07	9.65	8.23	
		$\bar{x}$	1.61±0.04	5.80±0.14	9.73±0.24	8.81±0.45	14.18±0.14
		B	2.67	3.68	11.50	8.53	19.23
			2.31	3.52	11.79	8.65	
		$\bar{x}$	2.49±0.18	3.60±0.08	11.65±0.15	8.59±0.06	19.23
		C	2.00	3.79	9.10	10.17	18.40
			1.95	4.01	8.99	10.32	
			1.77	4.49			
		$\bar{x}$	1.91±0.07	4.10±0.21	9.05±0.06	10.25±0.08	18.40
		Grand Mean	**2.00±0.26**	**4.50±0.67**	**10.14±0.78**	**9.22±0.52**	**17.27±1.56**

TABLE C-4. RAW DATA TABLES OF OXYGEN CONSUMPTION RATES (mL O_2 m^{-2} hr^{-1}) CALCULATED FROM INDIVIDUAL WATER SAMPLES TAKEN FROM REPLICATE CORES (MEANS ± 1 STD. ERROR OF MEAN SHOWN).

TREATMENT Cuttings(mm)	Sediment	REPLICATE CORE		SAMPLING DAY 1	3	7	15	30
5	Fine	A		2.79	2.61	8.86	12.38	15.18
				2.67	4.16	9.13	12.20	14.51
				2.79		9.54	12.50	14.81
			$\bar{x}$	2.75±0.05	3.39±0.78	9.18±0.20	12.36±0.09	14.83±0.19
		B		2.73	3.72	7.51	9.93	14.08
				2.92	3.29	7.63	10.55	14.34
						7.57		13.82
			$\bar{x}$	2.83±0.10	3.51±0.22	7.57±0.03	10.24±0.31	14.08±0.15
		C		2.98	3.16			13.96
				4.34	2.85			14.02
				3.60				13.83
			$\bar{x}$	3.64±0.68	3.01±0.16			13.94±0.06
		Grand Mean		**3.07±0.28**	**3.35±0.10**	**8.38±0.81**	**11.30±1.06**	**14.28±0.28**
5	Coarse	A		2.27	2.97	4.68	4.41	11.55
				2.27	2.65	4.56	4.59	11.35
						4.80		10.95
			$\bar{x}$	2.27±0.00	2.81±0.16	4.68±0.07	4.50±0.09	11.28±0.18
		B		2.34	1.96	8.19	3.23	11.34
				2.59		8.26	3.54	11.01
						8.19		
			$\bar{x}$	2.47±0.13	1.96	8.21±0.02	3.39±0.16	11.18±0.17
		C		3.16	3.60	5.59	10.30	11.68
				2.21		6.83	10.42	11.54
				3.03			10.30	
			$\bar{x}$	2.80±0.30	3.60	6.21±0.62	10.34±0.04	11.61±0.07
		Grand Mean		**2.51±0.15**	**2.97±0.47**	**6.37±1.02**	**6.08±2.16**	**11.36±0.13**

TABLE C-5. RAW DATA TABLES OF OXYGEN CONSUMPTION RATES (mL O_2 m^{-2} hr^{-1}) CALCULATED FROM INDIVIDUAL WATER SAMPLES TAKEN FROM REPLICATE CORES (MEANS ± 1 STD. ERROR OF MEAN SHOWN).

TREATMENT Cuttings(mm)	Sediment	REPLICATE CORE		SAMPLING DAY 1	3	7	15	30
15	Fine	A		4.83	3.29	7.68	11.36	10.10
				5.08	3.62	7.94	9.08	10.29
					2.87	7.91		10.18
			$\bar{x}$	4.96±0.13	3.26±0.22	7.84±0.08	10.22±1.14	10.19±0.06
		B		5.15	3.60	8.21	9.91	12.12
				5.25	3.78		10.18	11.99
					3.74		9.72	11.91
			$\bar{x}$	5.20±0.05	3.71±0.05	8.21	9.94±0.13	12.01±0.06
		C		4.78	4.10	7.98	10.81	10.73
				6.03	3.84		10.68	10.69
					3.88			
			$\bar{x}$	5.41±0.63	3.94±0.08	7.98	10.75±0.07	10.71±0.02
		Grand Mean		**5.19±0.13**	**3.64±0.20**	**8.01±0.11**	**10.30±0.24**	**10.97±0.54**
15	Coarse	A		2.48	4.89	8.23	11.06	9.50
				2.63		7.64	10.98	9.13
							10.86	
			$\bar{x}$	2.55±0.09	4.89	7.94±0.30	10.97±0.06	9.32±0.19
		B		2.98	4.06	9.03	11.53	9.03
				2.74	4.06	9.10	11.32	8.96
						9.21	11.36	
			$\bar{x}$	2.86±0.12	4.06±0.00	9.11±0.05	11.40±0.06	9.00±0.04
		C		2.26	0.40	9.32	10.22	9.36
					0.58	9.45	10.18	9.32
					0.84	9.15	8.89	9.00
			$\bar{x}$	2.26	0.61±0.13	9.31±0.09	9.76±0.44	9.23±0.11
		Grand Mean		**2.56±0.17**	**3.19±1.31**	**8.79±0.43**	**10.71±0.49**	**9.18±0.10**

TABLE C-6. SUMMARY OF OXYGEN CONSUMPTION RATES FOR EACH TREATMENT (MEAN ± 1 STD. ERROR OF MEAN, N=3 CORES)

TANK		SAMPLING DAY 1	3	7	15	30
0mm	Fine	1.04±0.16	4.29±0.58	6.52±0.43	3.73±0.11	4.53±0.62
0	Coarse	-0.13±0.13	1.15±0.12	1.48±0.30	0.93±0.10	4.14±1.33
1	Fine	3.81±0.29	3.35±0.30		10.35±0.39	12.11±0.28
1	Coarse	3.05±0.32	2.15±0.17		11.64±0.42	8.98±0.51
2.5	Fine	2.85±0.20	4.57±0.98	9.90±0.26	10.86±0.07	15.24±0.26
2.5	Coarse	2.00±0.26	4.50±0.67	10.14±0.78	9.22±0.52	17.27±1.56
5	Fine	3.07±0.28	3.35±0.10	8.38±0.81	11.30±1.06	14.28±0.28
5	Coarse	2.51±0.15	2.97±0.47	6.37±1.02	6.08±2.16	11.36±0.13
15	Fine	5.19±0.13	3.64±0.20	8.01±0.11	10.30±0.24	10.97±0.54
15	Coarse	2.56±0.17	3.19±1.31	8.79±0.43	10.71±0.49	9.18±0.10